



09/856396
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By appointment to
Her Majesty Queen Elizabeth II,
manufacturers of photographic supplies,
Kodak Limited, Hemel Hempstead

NOV 07 2000

PATENT LEGAL STAFF

02 November 2000

Ref: 11527/79888/04

ENTERED IN
MASTER

European Patent Office,
Erhardtstrasse 27,
D-80331 Munchen,
Germany.

Dear Sirs

INTERNATIONAL PATENT APPLICATION NO. PCT/GB99/04360
EASTMAN KODAK COMPANY : DOCKET 79888 /FEC

This is in response to the first Written Opinion of 11 August 2000 to which a reply is due by 11 November 2000.

The Examiner has raised five citations as apparently affecting the novelty of claims 1 to 7 and 10 to 12. No objection has been raised against claims 8 and 9.

The first of these has a single compound, coupler 25, which falls within the scope of claim 1 as filed. Claim 1 as amended does not include the possibility of the 'other' of Y and Z (see line 22 of claim 1) being an alkyl group other than a fluoro-substituted alkyl group. It has been found that, for satisfactory dye hue, it is preferred to have an aryl or heterocyclic group in this position but that fluoro-substitution of an alkyl group is similarly effective. Since R₂ in coupler 25 (i.e. X or Y) is an alkyl group substituted with a substituted aryloxy group, which would not provide the appropriate dye hue, this compound no longer falls within the scope of claim 1.

D2 has a single compound, compound 3, within the scope of unamended claim 1. This compound has a pyridyl group attached to the SO₂ group. Since R₂ in this instance is a substituted aryl group, as required by amended claim 1 for the other of X and Y, a proviso has been included to exclude compound 3 from the scope of amended claim 1. Thus in amended claim 1 when R₂ is an unsubstituted benzyl group, n is 1 and -N(R₂)SO₂R is in the ortho position, R may not be a pyridyl group.

PATENTS
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D3 and D4 disclose couplers 18 and 19 respectively each of which has the $-N(R_2SO_2R)$ substituent in the meta position. According to amended claim 1 such a substituent can only now be in the para position or in one or both of the ortho positions. These compounds no longer fall within the scope of claim 1.

It is believed that the newly restricted claim has the required novelty over the citations made. In accordance therewith the specification has been adapted to the amended claims, including the deletion of structures I-11 and I-12 therefrom.

As requested by the Examiner, with reference to Section VII, documents D1 to D3 and D5 have now been disclosed on page 2 of the specification and compliance made with the formal requirements detailed in paragraphs 2 and 3 thereof.

Regarding Section VIII, it is respectfully submitted that claim 4 does have clear support from the specification. Claim 4 claims 'an element according to any one of the preceding claims wherein R_1 is an alkyl group having at least 8 carbon atoms'. Page 5 lines 13 to 15 state that R_1 can be an unsubstituted or substituted alkyl group which can be a ballast group having at least 8 carbon atoms. (The passage continues on lines 17 and 18 that R_1 may more preferably have at least 12 carbon atoms).

Page 7 lines 4 to 18 describe the nature of the ballast group – it is such that sufficient bulk and aqueous insolubility are conferred on a coupler molecule so as to render the coupler substantially nondiffusible from the layer in which it is coated in the photographic element, and generally contains at least 8 carbon atoms. It is well known in the art that such a ballast group is often an alkyl group having at least 8 carbon atoms and as exemplified in coupler I-1 wherein R_1 is a $C_{12}H_{25}$ group. With respect the Applicant fails to see the nature of the Examiner's objection in this regard.

Objection has been raised against the independent nature of claim 10. This claim is not dependent upon claim 1 because it was not intended to be so dependent, reference back to claim 1 being for the purpose of rendering the claim clear and concise, avoiding unnecessary repetition. The Applicant wishes to retain this claim in its present format. It is believed that no objection will be raised during examination of the European application since it is conventional in photographic patents for independent claims to single and multilayer photographic elements to be contained in one and the same application, being linked by a single general inventive concept.

The Applicant has amended claim 1 to include the necessity for a ballast group to be present in one of the substituent groups R , R_1 , R_2 , X and Y or Z as requested by the Examiner and in line with the disclosure on page 5 lines 4-6.

Finally the Applicant has deleted coupler I-10 which the Examiner has correctly pointed out does not satisfy formula (I) of claim 1.

Amended pages 2,4,5,11,12,16,17,20,22,25 and 34-36 are enclosed herewith in triplicate, together with hand-amended pages showing the amendments made.

It is believed that the Applicant has satisfied all the objections raised in the Written Opinion and now looks forward to the receipt of the International Preliminary Examination report in due course.

Yours respectfully,

H C Haile

Mrs H C Haile
Authorised Representative (GA 251)
Tel (020) 8424 4419

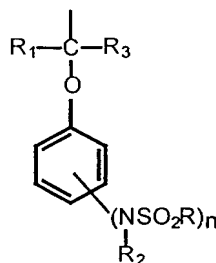
Enc. Amended pages 2,4,5,11,12,16,17,20,22,25 and 34-36
Hand-amended pages
cc. Eastman Kodak Company (fao AJA)

In recent years, a great deal of study has been conducted to improve image couplers for silver halide photosensitive materials in terms of improved colour reproducibility and image dye stability. However, further improvements are needed, particularly in the area of cyan couplers. In general, cyan dyes are formed
5 by the reaction of, generally, phenols or naphthols with oxidised colour developing agents as described, for example, in U.S. Patent Nos. 2,367,351, 2,423,730, 2,474,293, 2,772,161, 2,772,162, 2,895,826, 2,920,961, 3,002,836, 3,034, 892, 3,041,236, 3,466,622, 3,476,563, 3,552,962, 3,758,308, 3,779,763, 3,839,044, 3,880,661, 3,998,642, 4,214,396, 4,299,914, 4,362,810, 4,333,999,
10 4,883,746, 4,990,436, 4,960,685, 5,476,757 and 5,614,357; in French Patent Nos. 1,478,188 and 1,479,043, in UK Patent No. 2,070,000 and "Farbkuppler - Eine Literature Übersicht," published in Agfa Mitteilungen, Band III, pp. 156-175 (1961). Also useful are the cyan couplers described in, for instance, European Patent Application Nos. 544,322; 556,700; 556,777; 565,096; 570,006; and
15 574,948 and JP-A-59069755.

These types of image couplers can be used either by being incorporated in the photographic silver halide emulsion layers or externally in the processing baths. In the former case the couplers must have ballast substituents built into the molecule to prevent the couplers from migrating from one layer into another.
20 Although these couplers have been used extensively in colour photographic film and paper products, the dyes derived from them still suffer from poor stability to heat, humidity or light, low coupling efficiency or optical density, and in particular from undesirable blue and green absorptions which cause considerable reduction in colour reproduction and colour saturation.

25 2,5-diacylamino phenols are well known in the art of photography, and it is also well known that image dyes derived from them exhibit good resistance to fading by heat and humidity. However their image dyes are deficient in their ability to withstand the effects of light. Moreover, their absorption bands tend to lie at shorter wavelengths than is desirable, particularly for colour paper
30 applications.

one of Y and Z is the group



wherein

each R is independently an unsubstituted or substituted alkyl or aryl group or a
5 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from
nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted;

R₁ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

R₂ is an unsubstituted or substituted alkyl or aryl group or a 5-10 membered
heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen
10 and sulfur, which ring is unsubstituted or substituted;

R₃ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

n is 1 or 2, and each group -N(R₂)SO₂R is in the ortho or para position,

the other of Y and Z is a fluoro-substituted alkyl group or an unsubstituted or
substituted aryl group or a 5-10 membered heterocyclic ring which contains one or more
15 heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or
substituted, provided that (a) when R₂ is an unsubstituted benzyl group, n is 1 and
-N(R₂)SO₂R is in the ortho position, R may not be a pyridyl group, and (b) at least one of
R, R₁, R₂, X and Y or Z is or includes a ballast group.

In another embodiment of the invention there is provided a multicolour
20 photographic element comprising a support bearing yellow, magenta and cyan image-dye-
forming units comprising at least one blue-, green- or red-sensitive silver halide emulsion
layer having associated therewith at least one yellow, magenta or cyan dye-forming coupler
respectively, wherein the element comprises at least one cyan dye-forming coupler of
formula (I) as herein described.

25 In yet another embodiment of the invention there is provided a process of
forming an image in a photographic element as hereinbefore defined after the

element has been imagewise exposed to light, comprising contacting the element, as herein described, with a colour developing agent.

In a further embodiment of the invention there is provided a novel coupler of formula (I) as herein described.

5

Advantageous Effect of the Invention

This invention provides an element which yields a cyan image of good hue, with good stability to heat, humidity and light, whilst retaining the other properties desirable for good photographic performance.

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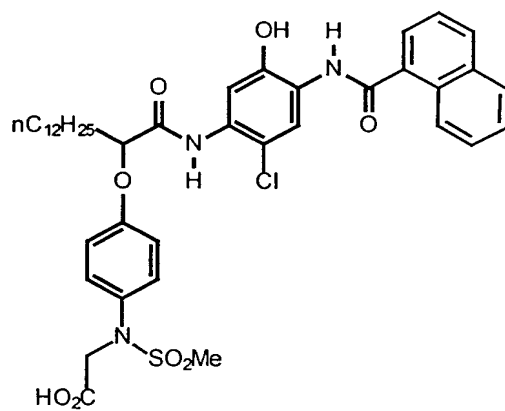
Detailed Description of the Invention

As used herein and throughout the specification unless where specifically stated otherwise, the term "alkyl" refers to an unsaturated or saturated, straight or branched chain alkyl group, including alkenyl and aralkyl, and includes cyclic alkyl groups, including cycloalkenyl, having 3-8 carbon atoms and the term "aryl" includes specifically fused aryl. The term "lower alkyl" refers to an alkyl group having up to 6 carbon atoms, preferably up to 4 carbon atoms.

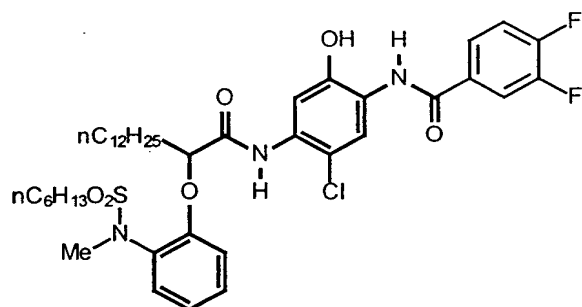
In a preferred embodiment of the invention R, R₁ and R₂ are independently an unsubstituted or substituted alkyl group, with at least one of these normally being a ballast group having at least 8 carbon atoms to render the coupler substantially nondiffusible from the layer in which it is coated. More preferably R and R₂ are lower alkyl groups, especially methyl or ethyl, and the ballast is provided in R₁, which may desirably contain at least 12 carbon atoms. Desirably R₃ is a hydrogen atom. Preferably n is 1 and the -N(R₂)SO₂R group is in the para position although it is possible for there to be one or two such groups in the ortho positions.

Preferably the group Z contains the -N(R₂SO₂R) substituent and the group Y is suitably an unsubstituted or substituted aryl group, which may provide a ballast residue, and is especially a phenyl group substituted, for example with one or more chloro, fluoro, trifluoromethyl, cyano, alkoxycarbonyl or alkylsulfonyl groups or it may be a naphthyl, pyridyl or a fluoro-substituted alkyl group.

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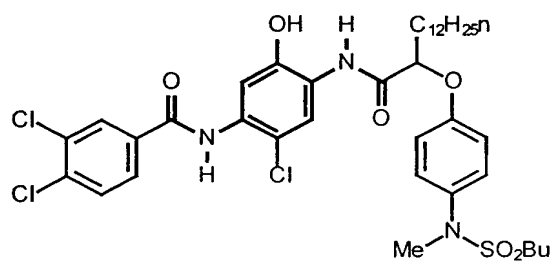


I-9



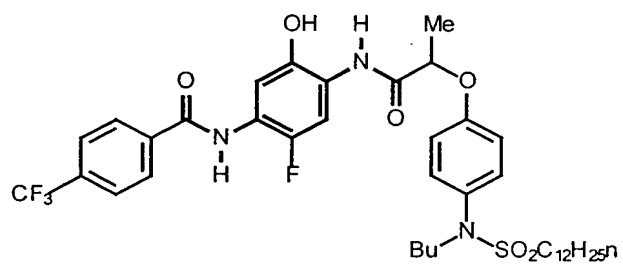
I-13

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1-14

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1-15

If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular substituents used may be selected by those skilled in the art to attain the desired photographic properties for a specific application and can include, for example, hydrophobic groups, solubilizing groups, blocking groups, releasing or releasable groups. Generally, the above groups and substituents thereof may include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected.

Representative substituents on ballast groups include alkyl, aryl, alkoxy, aryloxy, alkylthio, hydroxy, halogen, alkoxycarbonyl, aryloxycarbonyl, carboxy, acyl, acyloxy, amino, anilino, carbonamido, carbamoyl, alkylsulfonyl, arylsulfonyl, sulfonamido and sulfamoyl groups wherein the substituents typically contain 1 to 42 carbon atoms. Such substituents can also be further substituted.

The materials for use in the invention can be used in any of the ways and in any of the combinations known in the art. Typically, the materials are incorporated in a silver halide emulsion and the emulsion coated as a layer on a support to form part of a photographic element. Alternatively, unless provided otherwise, they can be incorporated at a location adjacent to the silver halide emulsion layer where, during development, they will be in reactive association with development products such as oxidised colour developing agent. Thus, as used herein, the term "associated" signifies that the compound is in the silver halide emulsion layer or in an adjacent location where, during processing, it is capable of reacting with silver halide development products.

The photographic elements can be single colour elements or multicolour elements. Multicolour elements contain image dye-forming units sensitive to each of the three primary regions of the spectrum. Each unit can comprise a single emulsion layer or multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer.

A typical multicolour photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layers, interlayers, overcoat layers and subbing layers.

In the following discussion of suitable materials for use in the emulsions and elements that can be used in conjunction with this photographic element, reference will be made to Research Disclosure, September 1996, Item 38957, published by Kenneth Mason Publications, Ltd., Dudley House, 12 North Street, Emsworth, Hampshire PO10 7DQ, England, which will be identified hereafter by the term "Research Disclosure" and the Sections hereafter referred to are Sections of this Research Disclosure.

The emulsions can be surface-sensitive emulsions, i.e. emulsions that form latent images primarily on the surfaces of the silver halide grains, or the emulsions can form internal latent images predominantly in the interior of the silver halide grains. The emulsions can be negative-working emulsions, such as surface-sensitive emulsions or unfogged internal latent image-forming emulsions, or direct-positive emulsions of the unfogged, internal latent image-forming type, which are positive-working when development is conducted with uniform light exposure or in the presence of a nucleating agent.

Suitable emulsions and their preparation as well as methods of chemical and spectral sensitisation are described in Sections I and III-IV. Vehicles and vehicle related addenda are described in Section II. Dye image formers and modifiers are described in Section X. Various additives such as UV dyes, brighteners, luminescent dyes, antifoggants, stabilizers, light absorbing and scattering materials, coating aids, plasticizers, lubricants, antistats and matting

The invention may be practised with any permanent high-boiling solvent known to be useful in the art, such as an aryl ester, such as dibutyl phthalate, diundecyl phthalate; phenols, such as p-dodecyl phenol, 2,4-di-isoamyl phenol: phosphates, such as trihexyl phosphate and tricresyl phosphate; alcohols, such as oleyl alcohol
5 and hexadecanol and amides such as diethyldodecanamide and dibutylacetanilide.

The resulting organic solution may then be mixed with an aqueous gelatin solution and the mixture passed through a mechanical mixing device suitable for high-shear or turbulent mixing generally suitable for preparing photographic emulsified dispersions, such as a colloid mill, homogenizer, microfluidizer, high-
10 speed mixer, ultrasonic dispersing apparatus, blade mixer, device in which a liquid stream is pumped at high pressure through an orifice or interaction chamber, Gaulin mill or blender to form small particles of the organic phase suspended in the aqueous phase. More than one type of device may be used to prepare the dispersions. The auxiliary organic solvent may then removed by evaporation,
15 noodle washing, or membrane dialysis. The dispersion particles preferably have an average particle size of less than $2\mu\text{m}$, generally from about 0.02 to $2\mu\text{m}$, more preferably from about 0.02 to $0.5\mu\text{m}$, especially from about 0.02 to $0.3\mu\text{m}$. These methods are described in detail in U.S. Patent Nos. 2,322,027, 2,787,544, 2,801,170, 2,801,171, 2,949,360 and 3,396,027.

20 Examples of suitable auxiliary solvents which can be used in the present invention include: ethyl acetate, isopropyl acetate, butyl acetate, ethyl propionate, 2-ethoxyethylacetate, 2-(2-butoxyethoxy) ethyl acetate, dimethylformamide, 2-methyl tetrahydrofuran, triethyl-phosphate, cyclohexanone, butoxyethyl acetate, methyl isobutyl ketone, methyl acetate, 4-methyl-2-pentanol, diethyl carbitol,
25 1,1,2-trichloroethane and 1,2-di-chloropropane.

The aqueous phase of the coupler dispersions for use in the invention preferably comprises gelatin as a hydrophilic colloid. This may be gelatin or a modified gelatin such as acetylated gelatin, phthalated gelatin or oxidized gelatin. Gelatin may be base-processed, such as lime-processed gelatin, or may be acid-
30 processed, such as acid-processed ossein gelatin. Other hydrophilic colloids may also

The materials for use in the invention may also be used in combination with filter dye layers comprising colloidal silver sol or yellow, cyan and/or magenta filter dyes, either as oil-in-water dispersions, latex dispersions or as solid particle dispersions. Additionally, they may be used with "smearing" couplers
5 (e.g. as described in U.S. Patent Nos. 4,366,237, 4,420,556, 4,543,323 and in EP 96,570) Also, the compositions may be blocked or coated in protected form as described, for example, in Japanese Application 61/258,249 or U.S. Patent No. 5,019,492.

The materials for use in the invention may further be used in combination
10 with image-modifying compounds such as "Developer Inhibitor-Releasing" compounds (DIRs). DIRs useful in conjunction with the compositions of the invention are known in the art and examples are described in U.S. Patent Nos. 3,137,578; 3,148,022; 3,148,062; 3,227,554; 3,384,657; 3,379,529; 3,615,506; 3,617,291; 3,620,746; 3,701,783; 3,733,201; 4,049,455; 4,095,984; 4,126,459;
15 4,149,886; 4,150,228; 4,211,562; 4,248,962; 4,259,437; 4,362,878; 4,409,323; 4,477,563; 4,782,012; 4,962,018; 4,500,634; 4,579,816; 4,607,004; 4,618,571; 4,678,739; 4,746,600; 4,746,601; 4,791,049; 4,857,447; 4,865,959; 4,880,342; 4,886,736; 4,937,179; 4,946,767; 4,948,716; 4,952,485; 4,956,269; 4,959,299; 4,966,835; 4,985,336 as well as in patent publications GB 1,560,240; GB
20 2,007,662; GB 2,032,914; GB 2,099,167; DE 2,842,063, DE 2,937,127; DE 3,636,824; DE 3,644,416 as well as the following European Patent Publications: 272,573; 335,319; 336,411; 346, 899; 362, 870; 365,252; 365,346; 373,382; 376,212; 377,463; 378,236; 384,670; 396,486; 401,612; 401,613.

Such compounds are also disclosed in "Developer-Inhibitor-Releasing
25 (DIR) Couplers for Color Photography," C.R. Barr, J.R. Thirtle and P.W. Vittum in Photographic Science and Engineering, Vol.13, p.174 (1969). Generally, the developer inhibitor-releasing (DIR) couplers include a coupler moiety and an inhibitor coupling-off moiety (IN). The inhibitor-releasing couplers may be of the time-delayed type (DIAR couplers) which also include a timing moiety or
30 chemical switch which produces a delayed release of inhibitor. Examples of typical inhibitor moieties are: oxazoles, thiazoles, diazoles, triazoles, oxadiazoles, thiadiazoles, oxathiazoles, thiatriazoles,

production of carbon dioxide, formaldehyde or other low molecular weight by-products. The groups are exemplified in EP 464,612, EP 523,451, U.S. 4,146,396, Japanese Kokai 60-249148 and 60-249149.

It is also contemplated that the concepts of the present invention may be employed to obtain reflection colour prints as described in Research Disclosure, November 1979, Item 18716, available from Kenneth Mason Publications, Ltd, Dudley Annex, 12a North Street, Emsworth, Hampshire P0101 7DQ, England. Materials of the invention may be coated on pH adjusted support as described in U.S. Patent No. 4,917,994; on a support with reduced oxygen permeability (EP 553,339); with epoxy solvents (EP 64,961); with nickel complex stabilisers (U.S. Patent Nos. 4,346,165, 4,540,653 and 4,906,559 for example); with ballasted chelating agents such as those in U.S. Patent No. 4,994,359 to reduce sensitivity to polyvalent cations such as calcium and with stain reducing compounds such as described in U.S. Patent No. 5,068,171. Other compounds useful in combination with the invention are disclosed in Japanese Published Applications described in Derwent Abstracts having accession numbers as follows: 90-072,629, 90-072,630; 90-072,631; 90-072,632; 90-072,633; 90-072,634; 90-077,822; 90-078,229; 90-078,230; 90-079,336; 90-079,337; 90-079,338; 90-079,690; 90-079,691; 90-080,487; 90-080,488; 90-080,489; 90-080,490; 90-080,491; 90-080,492; 90-080,494; 90-085,928; 90-086,669; 90-086,670; 90-087,360; 90-087,361; 90-087,362; 90-087,363; 90-087,364; 90-088,097; 90-093,662; 90-093,663; 90-093,664; 90-093,665; 90-093,666; 90-093,668; 90-094,055; 90-094,056; 90-103,409; 83-62,586 and 83-09,959.

Any silver halide combination can be used for the photographic element, such as silver chloride, silver chlorobromide, silver chlorobromiodide, silver bromide, silver bromiodide, or silver chloriodide. In cases where the emulsion composition is a mixed halide, the minor component may be added in the crystal formation or after formation as part of the sensitisation or melting. The shape of the silver halide emulsion grain can be cubic, pseudo-cubic, octahedral, tetradecahedral or tabular. The emulsions may be precipitated in any suitable

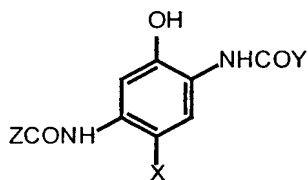
The results show that the couplers I-1 and I-2 of this invention are comparable in activity to the comparison couplers CC1 and CC2, and give dyes with adequately deep hue. The thermal dark stability of the image dye from the comparison coupler CC1 is good, and superior to that of the comparison coupler
5 CC2, but its light stability is poor. The dyes from the inventive couplers I-1 and I-2 retain the excellent dark stability displayed by the analogous dyes from CC1, and also demonstrate good light stability, superior to that of the image dye from CC2.

Comparison coupler CC2 is already well known as a commercially
10 important component of photographic colour paper products and the image dyes from the inventive couplers are superior to those of CC2 in terms of resistance to decomposition by both light and heat.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations
15 and modifications can be effected within the claims of the invention.

Claims:

1. A photographic element comprising at least one silver halide emulsion layer having associated therewith a phenolic cyan dye-forming coupler of formula (I)

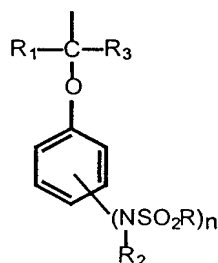


(I)

wherein

X is hydrogen or a group that can be split off by the reaction of the coupler with an oxidised colour developing agent, and

one of Y and Z is the group



wherein

each R is independently an unsubstituted or substituted alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted;

R₁ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

R₂ is an unsubstituted or substituted alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted;

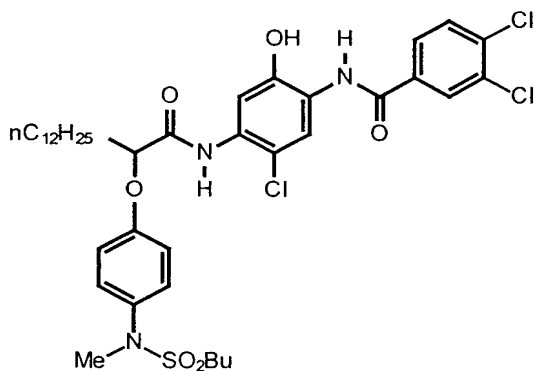
R₃ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

n is 1 or 2, and each group -N(R₂)SO₂R is in the ortho or para position,

the other of Y and Z is a fluoro-substituted alkyl group or an unsubstituted or substituted aryl group or a 5-10 membered heterocyclic ring which contains one or more



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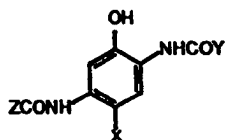




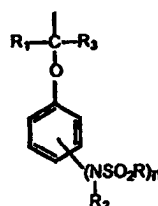
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : G03C 7/34, C07C 311/08	A1	(11) International Publication Number: WO 00/38013 (43) International Publication Date: 29 June 2000 (29.06.00)
(21) International Application Number: PCT/GB99/04360 (22) International Filing Date: 22 December 1999 (22.12.99) (30) Priority Data: 9828147.0 22 December 1998 (22.12.98) GB (71) Applicant (for all designated States except US): EASTMAN KODAK COMPANY [US/US]; 343 State Street, Rochester, NY 14650 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): CLARKE, David [GB/GB]; 19 Tavistock Road, Watford, Herts WD2 4HL (GB). LEYSHON, Llewellyn, J. [GB/GB]; 30 Stanbury Avenue, Watford, Herts WD1 3HW (GB). SMITH, Katie, E. [GB/GB]; 69 Coldharbour Lane, Bushey, Herts WD2 3NU (GB). (74) Agent: HAILE, H., C.; Kodak Limited, Headstone Drive, Harrow, Middx HA1 4TY (GB).		(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>

(54) Title: PHOTOGRAPHIC COUPLERS HAVING IMPROVED IMAGE DYE LIGHT STABILITY



(I)



(II)

(57) Abstract

There is provided a photographic element comprising at least one silver halide emulsion layer having associated therewith a novel phenolic cyan dye-forming coupler of formula (I), wherein X is hydrogen or a group that can be split off by the reaction of the coupler with an oxidised colour developing agent, and one of Y and Z is the group represented by formula (II), wherein each R is independently an unsubstituted or substituted alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted; R₁ is hydrogen or an unsubstituted or substituted alkyl or aryl group, R₂ is an unsubstituted or substituted alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted; R₃ is hydrogen or an unsubstituted or substituted alkyl or aryl group, n is 1 or 2, and the other of Y and Z is an unsubstituted or substituted alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted. The couplers for use in the element of the invention yield cyan images of good hue, with good stability to heat, humidity and light, whilst retaining the other properties desirable for good photographic performance.

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AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

PHOTOGRAPHIC COUPLERS HAVING IMPROVED IMAGE DYE LIGHT STABILITY

Field of the Invention

- 5 The present invention relates to a colour photographic element containing a novel phenolic cyan image dye-forming coupler and in particular a coupler containing an N-alkyl sulphonamide substituent.

Background of the invention

- 10 In silver halide based colour photography, a typical photographic element contains multiple layers of light-sensitive photographic silver halide emulsions coated on a support with one or more of these layers being spectrally sensitised to each of blue light, green light and red light. The blue, green and red light-sensitive layers typically contain yellow, magenta, and cyan image dye-forming
15 couplers, respectively. After exposure to light, colour development is accomplished by immersing the exposed material in an aqueous alkali solution containing an aromatic primary amine colour developing agent. The dye-forming couplers, hereinafter image couplers, are selected so as to react with the oxidised colour developing agent to provide yellow, magenta and cyan dyes in the so called
20 subtractive colour process to reproduce their complementary colours, blue, green and red as in the original image.

- The important features for selecting the image coupler include; efficient reaction with oxidised colour developing agent, thus minimising the necessary amounts of coupler and silver halide in the photographic element; the formation of
25 dyes with hues appropriate for the photographic use of interest: for colour photographic paper applications this requires that dyes have low unwanted side absorption leading to good colour reproduction in the photographic print; minimisation of image dye loss contributing to improved image permanence under both ambient illumination and conventional storage conditions; and in addition the
30 selected image coupler must exhibit good solubility in coupler solvents, provide good dispersibility in gelatin and remain stable during handling and manipulation for maximum efficiency in manufacturing processes.

In recent years, a great deal of study has been conducted to improve image couplers for silver halide photosensitive materials in terms of improved colour reproducibility and image dye stability. However, further improvements are needed, particularly in the area of cyan couplers. In general, cyan dyes are formed
5 by the reaction of, generally, phenols or naphthols with oxidised colour developing agents as described, for example, in U.S. Patent Nos. 2,367,351, 2,423,730, 2,474,293, 2,772,161, 2,772,162, 2,895,826, 2,920,961, 3,002,836, 3,034, 892, 3,041,236, 3,466,622, 3,476,563, 3,552,962, 3,758,308, 3,779,763, 3,839,044, 3,880,661, 3,998,642, 4,333,999, 4,883,746, 4,990,436, 4,960,685,
10 5,476,757 and 5,614,357; in French Patent Nos. 1,478,188 and 1,479,043, in UK Patent No. 2,070,000 and "Farbkuppler - Eine Literature Übersicht," published in Agfa Mitteilungen, Band III, pp. 156-175 (1961). Also useful are the cyan couplers described in, for instance, European Patent Application Nos. 544,322; 556,700; 556,777; 565,096; 570,006; and 574,948.

15 These types of image couplers can be used either by being incorporated in the photographic silver halide emulsion layers or externally in the processing baths. In the former case the couplers must have ballast substituents built into the molecule to prevent the couplers from migrating from one layer into another. Although these couplers have been used extensively in colour photographic film
20 and paper products, the dyes derived from them still suffer from poor stability to heat, humidity or light, low coupling efficiency or optical density, and in particular from undesirable blue and green absorptions which cause considerable reduction in colour reproduction and colour saturation.

25 2,5-diacylamino phenols are well known in the art of photography, and it is also well known that image dyes derived from them exhibit good resistance to fading by heat and humidity. However their image dyes are deficient in their ability to withstand the effects of light. Moreover, their absorption bands tend to lie at shorter wavelengths than is desirable, particularly for colour paper applications.

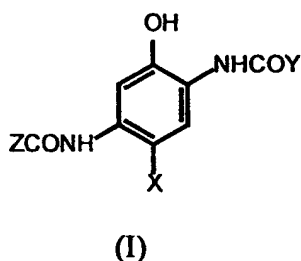
It is known that the absorption characteristics of image dyes can be manipulated by incorporating certain functionalities into the molecular structure and that the chemical environment in which the dye is situated can also influence the hue of the dye. For example, US 5,376,519 and JP 5,9171,953 teach the use of
5 certain phenolic coupler solvents to shift the dye absorption band to longer wavelengths.

Problem to be solved by the Invention

There is still a need to provide a photographic element containing a
10 dispersion of a cyan dye-forming coupler which can provide improved light and dark stability under normal storage conditions, improved colour reproduction in the generation of photographic images and high reactivity for formation of dye with oxidised colour developing agent.

15 Summary of the Invention

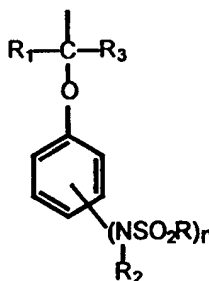
According to the present invention there is provided a photographic element comprising at least one silver halide emulsion layer having associated therewith a phenolic cyan dye-forming coupler of formula (I)



wherein

X is hydrogen or a group that can be split off by the reaction of the coupler with an oxidised colour developing agent, and

one of Y and Z is the group



wherein

each R is independently an unsubstituted or substituted alkyl or aryl group or a
5 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from
nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted;

R₁ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

R₂ is an unsubstituted or substituted alkyl or aryl group or a 5-10 membered
heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen
10 and sulfur, which ring is unsubstituted or substituted;

R₃ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

n is 1 or 2, and

the other of Y and Z is an unsubstituted or substituted alkyl or aryl group or a
5-10 membered heterocyclic ring which contains one or more heteroatoms selected from
15 nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted.

In another embodiment of the invention there is provided a multicolour
photographic element comprising a support bearing yellow, magenta and cyan image-dye-
forming units comprising at least one blue-, green- or red-sensitive silver halide emulsion
layer having associated therewith at least one yellow, magenta or cyan dye-forming coupler
20 respectively, wherein the element comprises at least one cyan dye-forming coupler of
formula (I) as herein described.

In yet another embodiment of the invention there is provided a process of
forming an image in a photographic element as hereinbefore defined after the
element has been imagewise exposed to light, comprising contacting the element,
25 as herein described, with a colour developing agent.

In a further embodiment of the invention there is provided a novel coupler
of formula (I) as herein described.

Advantageous Effect of the Invention

This invention provides an element which yields a cyan image of good hue, with good stability to heat, humidity and light, whilst retaining the other properties desirable for good photographic performance.

5

Detailed Description of the Invention

As used herein and throughout the specification unless where specifically stated otherwise, the term "alkyl" refers to an unsaturated or saturated, straight or branched chain alkyl group, including alkenyl and aralkyl, and includes cyclic alkyl groups, including cycloalkenyl, having 3-8 carbon atoms and the term "aryl" includes specifically fused aryl. The term "lower alkyl" refers to an alkyl group having up to 6 carbon atoms, preferably up to 4 carbon atoms.

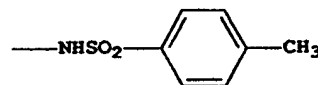
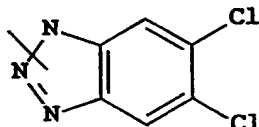
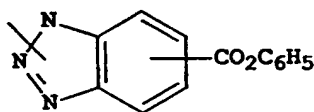
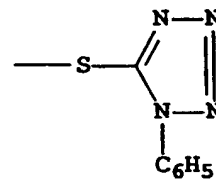
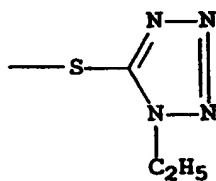
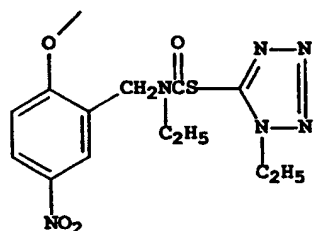
In a preferred embodiment of the invention R, R₁ and R₂ are independently an unsubstituted or substituted alkyl group, with at least one of these normally being a ballast group having at least 8 carbon atoms to render the coupler substantially nondiffusible from the layer in which it is coated. More preferably R and R₂ are lower alkyl groups, especially methyl or ethyl, and the ballast is provided in R₁, which may desirably contain at least 12 carbon atoms. Desirably R₃ is a hydrogen atom. Preferably n is 1 and the -N(R₂)SO₂R group is in the para position although it is possible for there to be one or two such groups in the ortho or meta positions.

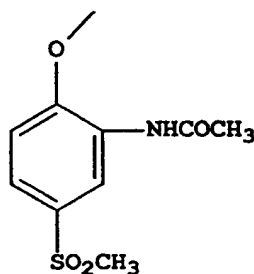
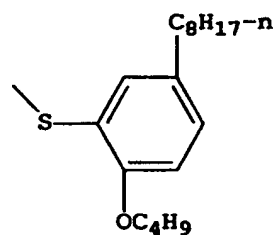
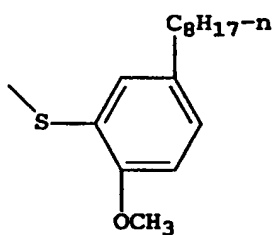
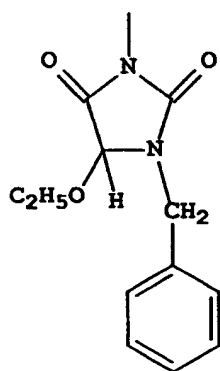
Preferably the group Z contains the N-alkylsulfonamido substituent and the group Y is suitably an unsubstituted or substituted aryl group, which may provide a ballast residue, and is especially a phenyl group substituted, for example with one or more chloro, fluoro, trifluoromethyl, cyano, alkoxycarbonyl or alkylsulfonyl groups or it may be a naphthyl, pyridyl or a fluoro-substituted alkyl group.

Couplers can be defined as being 4-equivalent or 2-equivalent depending on the number of atoms of Ag^+ required to form one molecule of dye. A 4-equivalent coupler can generally be converted into a 2-equivalent coupler by replacing a hydrogen at the coupling site with a different coupling-off group.

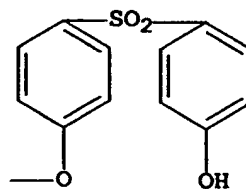
- 5 Coupling-off groups are well known in the art. Such groups can modify the reactivity of the coupler. Such groups can advantageously affect the layer in which the coupler is coated, or other layers in the photographic recording material, by performing, after release from the coupler, functions such as dye formation, dye hue adjustment, development acceleration or inhibition, bleach acceleration or
- 10 inhibition, electron transfer facilitation or colour correction. Representative classes of such coupling-off groups include, for example, chloro, alkoxy, aryloxy, heterooxy, sulfonyloxy, acyloxy, acyl, heterocyclyl, sulfonamido, mercapto-tetrazole, benzothiazole, alkylthio (such as mercaptopropionic acid), arylthio, phosphonyloxy and arylazo. These coupling-off groups are described in the art,
- 15 for example, in U.S. Pat. Nos. 2,455,169, 3,227,551, 3,432,521, 3,476,563, 3,617,291, 3,880,661, 4,052,212 and 4,134,766; and in U.K. Patents and published application Nos. 1,466,728, 1,531,927, 1,533,039, 2,006,755A and 2,017,704A, the disclosures of which are incorporated herein by reference. Halogen, alkoxy and aryloxy are most suitable.

- 20 Examples of suitable coupling-off groups are $-\text{Cl}$, $-\text{F}$, $-\text{Br}$, $-\text{SCN}$, $-\text{OCH}_3$, $-\text{OC}_6\text{H}_5$, $-\text{OCH}_2\text{C}(=\text{O})\text{NHCH}_2\text{CH}_2\text{OH}$, $-\text{OCH}_2\text{C}(\text{O})\text{NHCH}_2\text{CH}_2\text{OCH}_3$, $-\text{OCH}_2\text{C}(\text{O})\text{NHCH}_2\text{CH}_2\text{OC}(=\text{O})\text{OCH}_3$, $-\text{P}(=\text{O})(\text{OC}_2\text{H}_5)_2$, $-\text{SCH}_2\text{CH}_2\text{COOH}$,





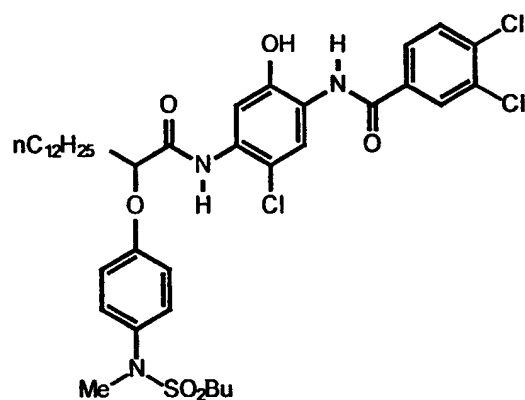
and



Typically the coupling-off group is a chlorine atom, hydrogen or a p-methoxy-phenoxy group.

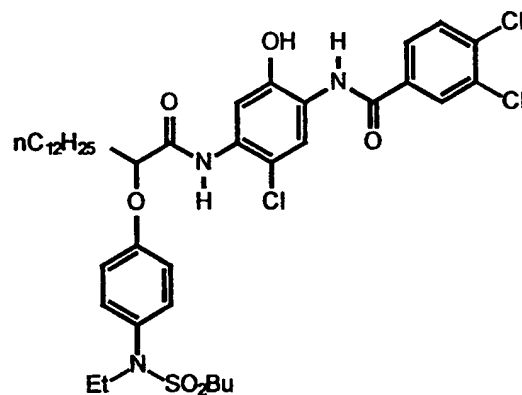
- It is important that the substituent groups R, R₁, R₂, X and Y or Z, are selected so as to adequately ballast the coupler and the resulting dye in the organic solvent in which the coupler is dispersed. The ballasting may be accomplished by providing hydrophobic substituent groups in one or more of these substituent groups. Generally a ballast group is an organic radical of such size and configuration as to confer on the coupler molecule sufficient bulk and aqueous insolubility as to render the coupler substantially nondiffusible from the layer in which it is coated in a photographic element. Thus the combination of these substituent groups in the couplers for use in the invention are suitably chosen to meet these criteria. To be effective, the ballast will usually contain at least 8 carbon atoms and typically contains 10 to 30 carbon atoms. Suitable ballasting may also be accomplished by providing a plurality of groups which in combination meet these criteria. Although the coupling-off group X may contain a ballast it is often necessary to ballast the other substituents as well, since X is eliminated from the molecule upon coupling.

The following examples further illustrate the invention. It is not to be construed that the present invention is limited to these examples:-



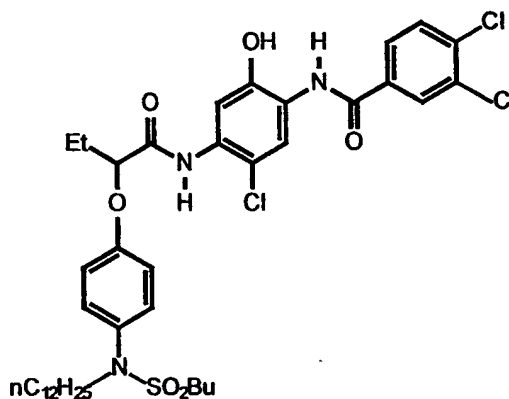
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I-1

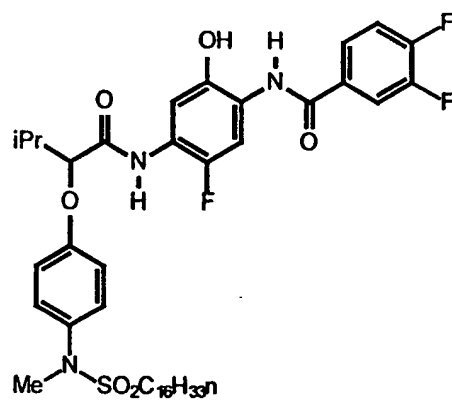


I-2

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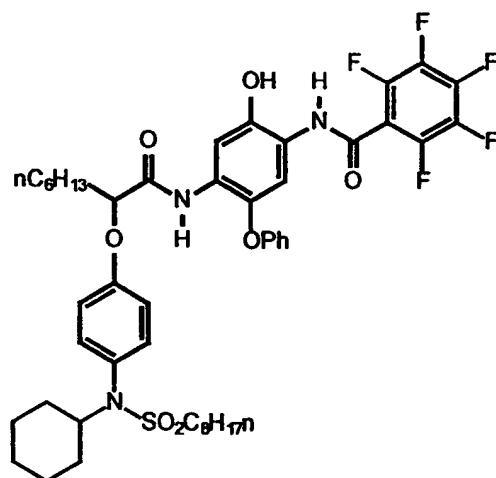
I-3



I-4

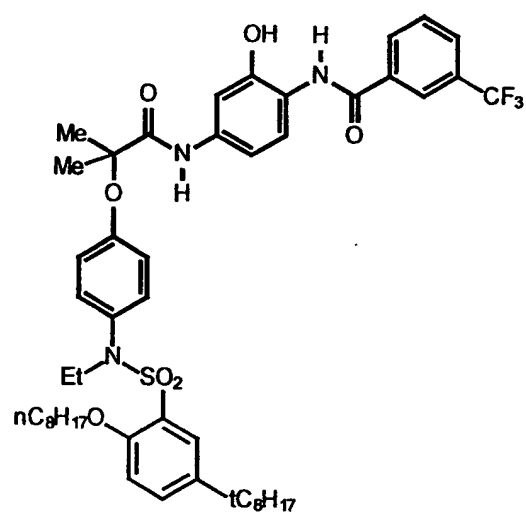
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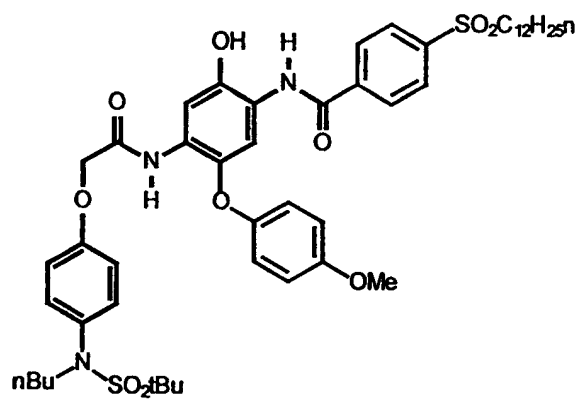
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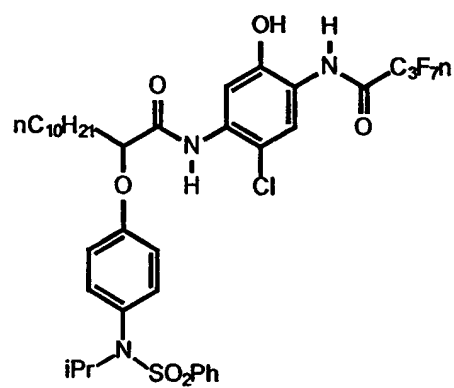
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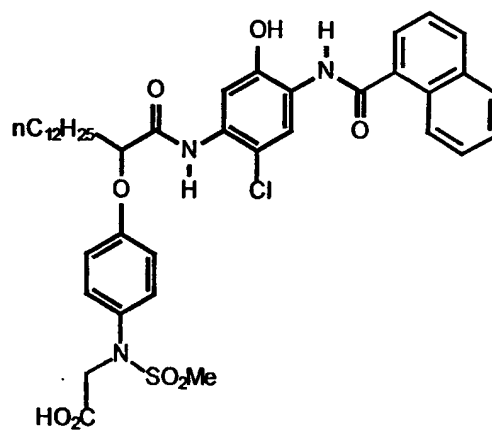


I-7

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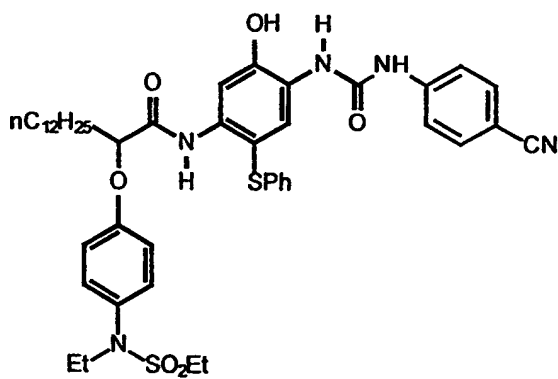


I-8



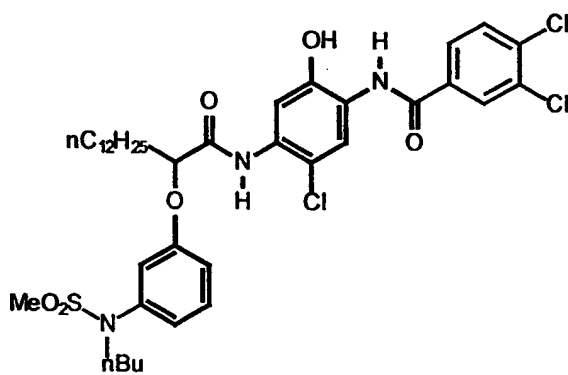
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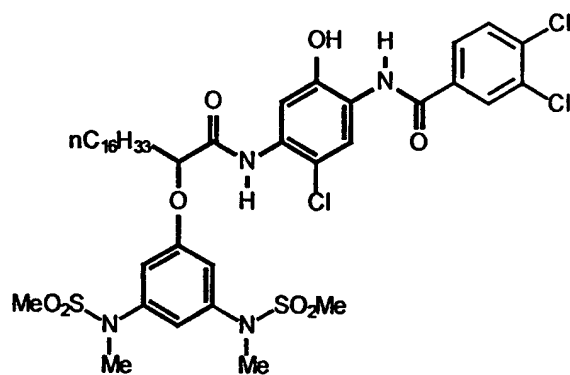
I-10

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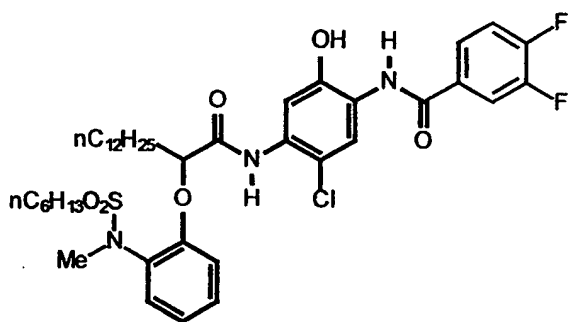


I-11

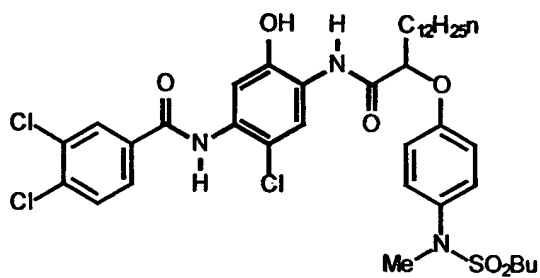
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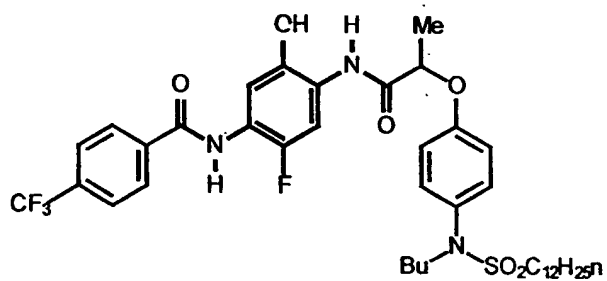
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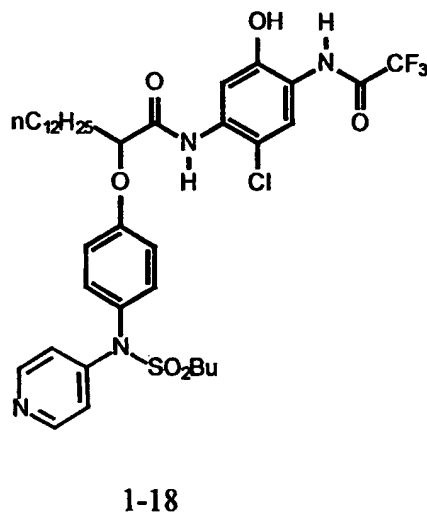
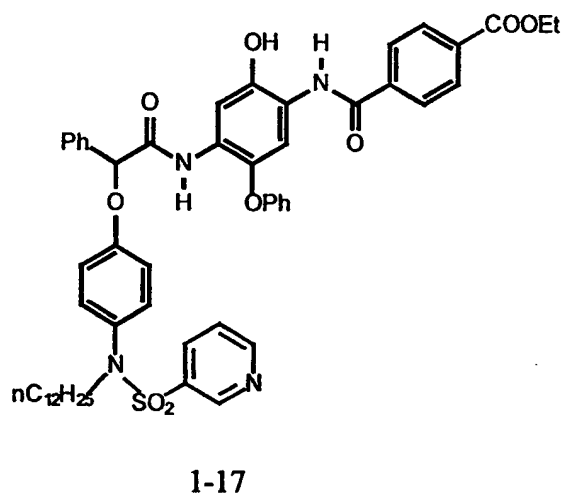
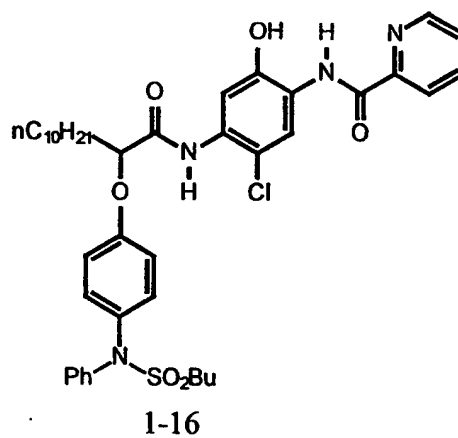
I-13



1-14



1-15



Unless otherwise specifically stated, substituent groups which may be substituted on molecules herein include any groups, whether substituted or unsubstituted, which do not destroy properties necessary for photographic utility. When the term "group" is applied to the identification of a substituent containing a substitutable hydrogen, it is intended to encompass not only the substituent's unsubstituted form, but also its form further substituted with any group or groups as herein mentioned. Suitably, the group may be halogen or may be bonded to the remainder of the molecule by an atom of carbon, silicon, oxygen, nitrogen, phosphorous or sulfur. The substituent may be, for example, halogen, such as chlorine, bromine or fluorine; nitro; hydroxyl; cyano; carboxyl; or groups which may be further substituted, such as alkyl, including straight or branched chain alkyl, such as methyl, trifluoromethyl, ethyl, *t*-butyl, 3-(2,4-di-*t*-pentylphenoxy) propyl and tetradecyl; alkenyl, such as ethylene, 2-butene; alkoxy, such as methoxy, ethoxy, propoxy, butoxy, 2-methoxyethoxy, *sec*-butoxy, hexyloxy, 2-ethylhexyloxy, tetradecyloxy, 2-(2,4-di-*t*-pentylphenoxy)ethoxy and 2-dodecyloxyethoxy; aryl such as phenyl, 4-*t*-butyl-phenyl, 2,4,6-trimethylphenyl, naphthyl; aryloxy, such as phenoxy, 2-methylphenoxy, alpha- or beta-naphthyl-oxy and 4-tolyloxy; carbonamido, such as acetamido, benzamido, butyramido, tetradecanamido, alpha-(2,4-di-*t*-pentylphenoxy)acetamido, alpha-(2,4-di-*t*-pentylphenoxy)butyramido, alpha-(3-pentadecylphenoxy)-hexanamido, alpha-(4-hydroxy-3-*t*-butylphenoxy)-tetradecanamido, 2-oxopyrrolidin-1-yl, 2-oxo-5-tetradecylpyrrolin-1-yl, N-methyltetradecanamido, N-succinimido, N-phthalimido, 2,5-dioxo-1-oxazolidinyl, 3-dodecyl-2,5-dioxo-1-imidazolyl and N-acetyl-N-dodecylamino, ethoxycarbonylamino, phenoxycarbonylamino, benzyloxy-carbonylamino, hexadecyloxy-carbonyl-amino, 2,4-di-*t*-butylphenoxy-carbonyl-amino, phenyl-carbonylamino, 2,5-(di-*t*-pentylphenyl)carbonylamino, *p*-dodecyl-phenylcarbonylamino, *p*-toluylcarbonylamino, N-methylureido, N,N-dimethyl-ureido, N-methyl-N-dodecyl-ureido, N-hexadecylureido, N,N-dioctadecylureido, N,N-dioctyl-N'-ethylureido, N-phenylureido, N,N-di-phenylureido, N-phenyl-N-*p*-toluylureido, N-(*m*-hexadecylphenyl)ureido, N,N-(2,5-di-*t*-pentylphenyl)-N'-ethylureido and *t*-butylcarbonamido; sulfonamido, such as methylsulfonamido, benzenesulfonamido, *p*-toluylsulfonamido, *p*-dodecylbenzenesulfonamido,

N-methyltetradecylsulfonamido, N,N-dipropylsulfamoylamino and hexadecylsulfonamido; sulfamoyl, such as N-methylsulfamoyl, N-ethylsulfamoyl, N,N-dipropylsulfamoyl, N-hexadecylsulfamoyl, N,N-dimethylsulfamoyl; N-[3-(dodecyloxy)propyl]sulfamoyl, N-[4-(2,4-di-*t*-pentylphenoxy)butyl]-sulfamoyl, N-methyl-N-tetradecyl-sulfamoyl and N-dodecylsulfamoyl; carbamoyl, such as N-methylcarbamoyl, N,N-dibutylcarbamoyl, N-octadecylcarbamoyl, N-[4-(2,4-di-*t*-pentylphenoxy)butyl]-carbamoyl, N-methyl-N-tetradecylcarbamoyl and N,N-di-octylcarbamoyl; acyl, such as acetyl, (2,4-di-*t*-amylphenoxy)acetyl, phenoxycarbonyl, *p*-dodecyloxyphenoxy-carbonyl, methoxycarbonyl, butoxycarbonyl, tetradecyl-oxycarbonyl, ethoxycarbonyl, benzyloxy-carbonyl, 3-pentadecyloxy carbonyl and dodecyloxy carbonyl; sulfonyl, such as methoxysulfonyl, octyloxysulfonyl, tetradecyloxysulfonyl, 2-ethylhexyloxy-sulfonyl, phenoxysulfonyl, 2,4-di-*t*-pentylphenoxysulfonyl, methylsulfonyl, octylsulfonyl, 2-ethylhexylsulfonyl, dodecylsulfonyl, hexadecylsulfonyl, phenylsulfonyl, 4-nonylphenylsulfonyl and *p*-toluylsulfonyl; sulfonyl-oxy, such as dodecylsulfonyloxy and hexadecylsulfonyl-oxy; sulfinyl, such as methylsulfinyl, octylsulfinyl, 2-ethylhexylsulfinyl, dodecylsulfinyl, hexadecyl-sulfinyl, phenylsulfinyl, 4-nonylphenylsulfinyl and *p*-toluylsulfinyl; thio, such as ethylthio, octylthio, benzylthio, tetradecylthio, 2-(2,4-di-*t*-pentylphenoxy)ethylthio, phenylthio, 2-butoxy-5-*t*-octylphenylthio and *p*-tolylthio; acyloxy, such as acetyloxy, benzoyloxy, octadecanoyloxy, *p*-dodecylamidobenzoyloxy, N-phenylcarbamoyloxy, N-ethylcarbamoyloxy and cyclohexyl-carbonyloxy; amino, such as phenylanilino, 2-chloro-anilino, diethylamino and dodecylamino; imino, such as 1 (N-phenylimido)ethyl, N-succinimido or 3-benzyl-hydantoinyl; phosphate, such as dimethylphosphate and ethylbutylphosphate; phosphite, such as diethyl and dihexylphosphite; a heterocyclic group, a heterocyclic oxy group or a heterocyclic thio group, each of which may be substituted and which contain a 3 to 7 membered heterocyclic ring composed of carbon atoms and at least one hetero atom selected from the group consisting of oxygen, nitrogen and sulfur, such as 2-furyl, 2-thienyl, 2-benzimidazolyloxy or 2-benzothiazolyl; quaternary ammonium, such as triethylammonium; and silyloxy, such as trimethylsilyloxy.

If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular substituents used may be selected by those skilled in the art to attain the desired photographic properties for a specific application and can include, for example, hydrophobic groups, solubilizing groups, blocking groups, releasing or releasable groups. Generally, the above groups and substituents thereof may include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected.

Representative substituents on ballast groups include alkyl, aryl, alkoxy, aryloxy, alkylthio, hydroxy, halogen, alkoxycarbonyl, aryloxy carbonyl, carboxy, acyl, acyloxy, amino, anilino, carbonamido, carbamoyl, alkylsulfonyl, arylsulfonyl, sulfonamido and sulfamoyl groups wherein the substituents typically contain 1 to 42 carbon atoms. Such substituents can also be further substituted.

The materials of the invention can be used in any of the ways and in any of the combinations known in the art. Typically, the invention materials are incorporated in a silver halide emulsion and the emulsion coated as a layer on a support to form part of a photographic element. Alternatively, unless provided otherwise, they can be incorporated at a location adjacent to the silver halide emulsion layer where, during development, they will be in reactive association with development products such as oxidised colour developing agent. Thus, as used herein, the term "associated" signifies that the compound is in the silver halide emulsion layer or in an adjacent location where, during processing, it is capable of reacting with silver halide development products.

The photographic elements can be single colour elements or multicolour elements. Multicolour elements contain image dye-forming units sensitive to each of the three primary regions of the spectrum. Each unit can comprise a single emulsion layer or multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer.

A typical multicolour photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver
5 halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layers, interlayers, overcoat layers and subbing layers.

10 In the following discussion of suitable materials for use in the emulsions and elements that can be used in conjunction with this photographic element, reference will be made to Research Disclosure, September 1996, Item 38957, published by Kenneth Mason Publications, Ltd., Dudley House, 12 North Street, Emsworth, Hampshire PO10 7DQ, England, which will be identified hereafter by
15 the term "Research Disclosure." The contents of the Research Disclosure, including the patents and publications referenced therein, are incorporated herein by reference, and the Sections hereafter referred to are Sections of the Research Disclosure.

The emulsions can be surface-sensitive emulsions, i.e. emulsions that form
20 latent images primarily on the surfaces of the silver halide grains, or the emulsions can form internal latent images predominantly in the interior of the silver halide grains. The emulsions can be negative-working emulsions, such as surface-sensitive emulsions or unfogged internal latent image-forming emulsions, or direct-positive emulsions of the unfogged, internal latent image-forming type,
25 which are positive-working when development is conducted with uniform light exposure or in the presence of a nucleating agent.

Suitable emulsions and their preparation as well as methods of chemical and spectral sensitisation are described in Sections I and III-IV. Vehicles and vehicle related addenda are described in Section II. Dye image formers and
30 modifiers are described in Section X. Various additives such as UV dyes, brighteners, luminescent dyes, antifoggants, stabilizers, light absorbing and scattering materials, coating aids, plasticizers, lubricants, antistats and matting

agents are described, for example, in Sections VI-IX. Layers and layer arrangements, colour negative and colour positive features, scan facilitating features, supports, exposure and processing can be found in Sections XI-XX.

Other image dye-forming couplers may be included in the element of the invention, including other couplers that form cyan dyes, such as are hereinbefore described. Preferably such couplers are phenols and naphthols that form cyan dyes on reaction with oxidised colour developing agent.

Couplers that form magenta dyes upon reaction with oxidised colour developing agent are described in such representative patents and publications as:

10 U.S. Pat. Nos. 2,600,788; 2,369,489; 2,343,703; 2,311,082; 2,908,573; 3,062,653; 3,152,896; 3,519,429 and "Farbkuppler - Eine Literature Übersicht," published in Agfa Mitteilungen, Band III, pp. 126-156 (1961). Preferably such couplers are pyrazolones, pyrazolotriazoles, or pyrazolobenzimidazoles that form magenta dyes upon reaction with oxidised colour developing agents. Especially preferred

15 couplers are 1H-pyrazolo [5,1-c]-1,2,4-triazole and 1H-pyrazolo [1,5-b]-1,2,4-triazole. Examples of 1H-pyrazolo [5,1-c]-1,2,4-triazole couplers are described in U.K. Patent Nos. 1,247,493; 1,252,418; 1,398,979; U.S. Patent Nos. 4,443,536; 4,514,490; 4,540,654; 4,590,153; 4,665,015; 4,822,730; 4,945,034; 5,017,465; and 5,023,170. Examples of 1H-pyrazolo [1,5-b]-1,2,4-triazoles can be found in

20 European Patent applications 176,804; 177,765; U.S Patent Nos. 4,659,652; 5,066,575; and 5,250,400.

Couplers that form yellow dyes upon reaction with oxidised and colour developing agent are described in such representative patents and publications as:

U.S. Pat. Nos. 2,875,057; 2,407,210; 3,265,506; 2,298,443; 3,048,194; 3,447,928;

25 3,960,570; 4,910,126 and 5,340,703 and "Farbkuppler - Eine Literature Übersicht," published in Agfa Mitteilungen, Band III, pp. 112-126 (1961). Such couplers are typically open chain ketomethylene compounds. Also preferred are yellow couplers such as described in, for example, European Patent Application Nos. 482,552; 510,535; 524,540; 543,367; and U.S. Patent No. 5,238,803. For

30 improved colour reproduction, couplers which give yellow dyes that cut off sharply on the long wavelength side are particularly preferred (for example, see U.S. Patent No. 5,360,713).

Couplers that form colourless products upon reaction with oxidised colour developing agent are described in such representative patents as: U.K. Patent No. 861,138; U.S. Patent Nos. 3,632,345, 3,928,041, 3,958,993 and 3,961,959.

Typically such couplers are cyclic carbonyl containing compounds that form
5 colourless products on reaction with an oxidised colour developing agent.

Couplers that form black dyes upon reaction with oxidised colour developing agent are described in such representative patents as U.S. Patent Nos. 1,939,231; 2,181,944; 2,333,106 and 4,126,461; German OLS No. 2,644,194 and German OLS No. 2,650,764. Typically, such couplers are resorcinols or m-
10 aminophenols that form black or neutral products on reaction with oxidised colour developing agent.

In addition to the foregoing, so-called "universal" or "washout" couplers may be employed. These couplers do not contribute to image dye-formation. Thus, for example, a naphthol having an unsubstituted carbamoyl or one
15 substituted with a low molecular weight substituent at the 2- or 3- position may be employed. Couplers of this type are described, for example, in U.S. Patent Nos. 5,026,628, 5,151,343 and 5,234,800.

It may be useful to use additional couplers any of which may contain known ballasts or coupling-off groups such as those described in U.S. Patent Nos.
20 4,301,235, 4,853,319 and 4,351,897. The coupler may contain solubilising groups such as described in U.S. Patent No. 4,482,629. The coupler may also be used in association with "wrong" coloured couplers (e.g. to adjust levels of interlayer correction) and, in colour negative applications, with masking couplers such as those described in EP 213,490; Japanese Published Application 58-172,647; U.S.
25 Patent Nos. 2,983,608, 4,070,191 and 4,273,861; German Applications DE 2,706,117 and DE 2,643,965; UK Patent No. 1,530,272 and Japanese Application 58-113935. The masking couplers may be shifted or blocked, if desired.

Typically, couplers are incorporated in a silver halide emulsion layer in a mole ratio to silver of 0.05 to 1.0 and generally 0.1 to 0.5. Usually the couplers
30 are dispersed in a high-boiling organic solvent in a weight ratio of solvent to coupler of 0.1 to 10.0 and typically 0.1 to 2.0, although dispersions using no permanent coupler solvent are sometimes employed.

The invention may be practised with any permanent high-boiling solvent known to be useful in the art, such as an aryl ester, such as dibutyl phthalate, diundecyl phthalate; phenols, such as p-dodecyl phenol, 2,4-di-isoamyl phenol; phosphates, such as trihexyl phosphate and tricresyl phosphate; alcohols, such as
5 oleyl alcohol and hexadecanol and amides such as diethyldodecanamide and dibutylacetanilide.

The resulting organic solution may then be mixed with an aqueous gelatin solution and the mixture passed through a mechanical mixing device suitable for high-shear or turbulent mixing generally suitable for preparing photographic
10 emulsified dispersions, such as a colloid mill, homogenizer, microfluidizer, high-speed mixer, ultrasonic dispersing apparatus, blade mixer, device in which a liquid stream is pumped at high pressure through an orifice or interaction chamber, Gaulin mill or blender to form small particles of the organic phase suspended in the aqueous phase. More than one type of device may be used to prepare the
15 dispersions. The auxiliary organic solvent may then be removed by evaporation, noodle washing, or membrane dialysis. The dispersion particles preferably have an average particle size of less than $2\mu\text{m}$, generally from about 0.02 to $2\mu\text{m}$, more preferably from about 0.02 to $0.5\mu\text{m}$, especially from about 0.02 to $0.3\mu\text{m}$. These methods are described in detail in U.S. Patent Nos. 2,322,027, 2,787,544,
20 2,801,170, 2,801,171, 2,949,360 and 3,396,027, the disclosures of which are incorporated by reference herein.

Examples of suitable auxiliary solvents which can be used in the present invention include: ethyl acetate, isopropyl acetate, butyl acetate, ethyl propionate, 2-ethoxyethylacetate, 2-(2-butoxyethoxy) ethyl acetate, dimethylformamide,
25 2-methyl tetrahydrofuran, triethyl-phosphate, cyclohexanone, butoxyethyl acetate, methyl isobutyl ketone, methyl acetate, 4-methyl-2-pentanol, diethyl carbitol, 1,1,2-trichloroethane and 1,2-di-chloropropane.

The aqueous phase of the coupler dispersions for use in the invention preferably comprises gelatin as a hydrophilic colloid. This may be gelatin or a
30 modified gelatin such as acetylated gelatin, phthalated gelatin or oxidized gelatin. Gelatin may be base-processed, such as lime-processed gelatin, or may be acid-processed, such as acid-processed ossein gelatin. Other hydrophilic colloids may also

be used, such as a water-soluble polymer or copolymer including, but not limited to poly(vinyl alcohol), partially hydrolyzed poly(vinyl acetate-co-vinyl alcohol), hydroxyethyl cellulose, poly(acrylic acid), poly(1-vinylpyrrolidone), poly(sodium styrene sulfonate), poly(2-acrylamido-2-methane sulfonic acid) and polyacrylamide.

- 5 Copolymers of these polymers with hydrophobic monomers may also be used.

A surfactant may be present in either the aqueous phase or the organic phase or the dispersions can be prepared without any surfactant present.

- Surfactants may be cationic, anionic, zwitterionic or non-ionic. Ratios of surfactant to liquid organic solution typically are in the range of 0.5 to 25 wt.% for forming small particle photographic dispersions. In a preferred embodiment of the invention, an anionic surfactant is contained in the aqueous gelatin solution. Particularly preferred surfactants which are employed in the present invention include an alkali metal salt of an alkarylene sulfonic acid, such as the sodium salt of dodecyl benzene sulfonic acid or sodium salts of isopropyl naphthalene sulfonic acids, such as mixtures of di-isopropyl- and tri-isopropyl naphthalene sodium sulfonates; an alkali metal salt of an alkyl sulfuric acid, such as sodium dodecyl sulfate; or an alkali metal salt of an alkyl sulfosuccinate, such as sodium bis (2-ethylhexyl) succinic sulfonate.
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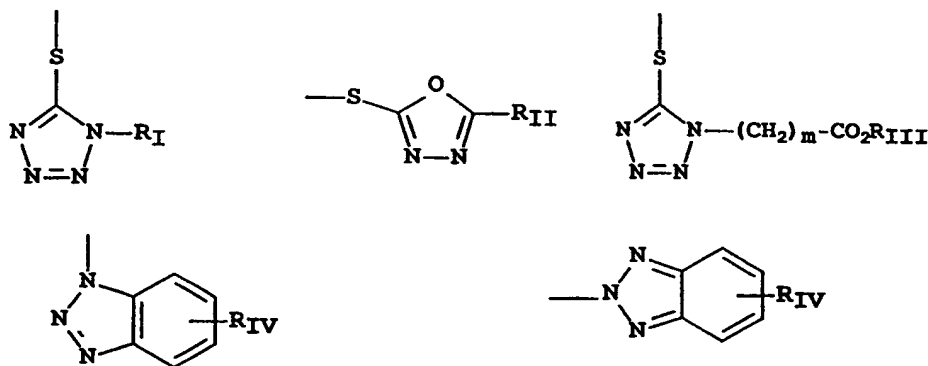
- The materials for use in the invention may be used in association with materials that accelerate or otherwise modify the processing steps e.g. of bleaching or fixing to improve the quality of the image. Bleach accelerator releasing couplers such as those described in EP 193,389; EP 301,477 and in U.S. Patent Nos. 4,163,669, 4,865,956 and 4,923,784, may be useful. Also contemplated is use of the compositions in association with nucleating agents, development accelerators or their precursors (UK Patent Nos. 2,097,140 and 2,131,188); electron transfer agents (U.S. Patent Nos. 4,859,578 and 4,912,025); antifogging and anti colour-mixing agents such as derivatives of hydroquinones, aminophenols, amines, gallic acid; catechol; ascorbic acid; hydrazides; sulfonamidophenols and non colour-forming couplers.
- 20
- 25

The materials for use in the invention may also be used in combination with filter dye layers comprising colloidal silver sol or yellow, cyan and/or magenta filter dyes, either as oil-in-water dispersions, latex dispersions or as solid particle dispersions. Additionally, they may be used with "smearing" couplers
5 (e.g. as described in U.S. Patent Nos. 4,366,237, 4,420,556, 4,543,323 and in EP 96,570) Also, the compositions may be blocked or coated in protected form as described, for example, in Japanese Application 61/258,249 or U.S. Patent No. 5,019,492.

The invention materials may further be used in combination with image-
10 modifying compounds such as "Developer Inhibitor-Releasing" compounds (DIRs). DIRs useful in conjunction with the compositions of the invention are known in the art and examples are described in U.S. Patent Nos. 3,137,578; 3,148,022; 3,148,062; 3,227,554; 3,384,657; 3,379,529; 3,615,506; 3,617,291; 3,620,746; 3,701,783; 3,733,201; 4,049,455; 4,095,984; 4,126,459; 4,149,886;
15 4,150,228; 4,211,562; 4,248,962; 4,259,437; 4,362,878; 4,409,323; 4,477,563; 4,782,012; 4,962,018; 4,500,634; 4,579,816; 4,607,004; 4,618,571; 4,678,739; 4,746,600; 4,746,601; 4,791,049; 4,857,447; 4,865,959; 4,880,342; 4,886,736; 4,937,179; 4,946,767; 4,948,716; 4,952,485; 4,956,269; 4,959,299; 4,966,835; 4,985,336 as well as in patent publications GB 1,560,240; GB 2,007,662; GB
20 2,032,914; GB 2,099,167; DE 2,842,063, DE 2,937,127; DE 3,636,824; DE 3,644,416 as well as the following European Patent Publications: 272,573; 335,319; 336,411; 346, 899; 362, 870; 365,252; 365,346; 373,382; 376,212; 377,463; 378,236; 384,670; 396,486; 401,612; 401,613.

Such compounds are also disclosed in "Developer-Inhibitor-Releasing
25 (DIR) Couplers for Color Photography," C.R. Barr, J.R. Thirtle and P.W. Vittum in Photographic Science and Engineering, Vol.13, p.174 (1969), incorporated herein by reference. Generally, the developer inhibitor-releasing (DIR) couplers include a coupler moiety and an inhibitor coupling-off moiety (IN). The inhibitor-releasing couplers may be of the time-delayed type (DIAR couplers) which also
30 include a timing moiety or chemical switch which produces a delayed release of inhibitor. Examples of typical inhibitor moieties are: oxazoles, thiazoles, diazoles, triazoles, oxadiazoles, thiadiazoles, oxathiazoles, thiatriazoles,

benzotriazoles, tetrazoles, benzimidazoles, indazoles, isoindazoles, mercapto-
 tetrazoles, selenotetrazoles, mercaptobenzothiazoles, selenobenzothiazoles,
 mercaptobenzoxazoles, selenobenzoxazoles, mercaptobenzimidazoles, seleno-
 benzimidazoles, benzodiazoles, mercaptooxazoles, mercapthiadiazoles,
 5 mercapthiazoles, mercaptotriazoles, mercaptooxadiazoles, mercaptodiazoles,
 mercaptooxathiazoles, tellurotetrazoles or benzisodiazoles. In a preferred
 embodiment, the inhibitor moiety or group is selected from the following
 formulae:



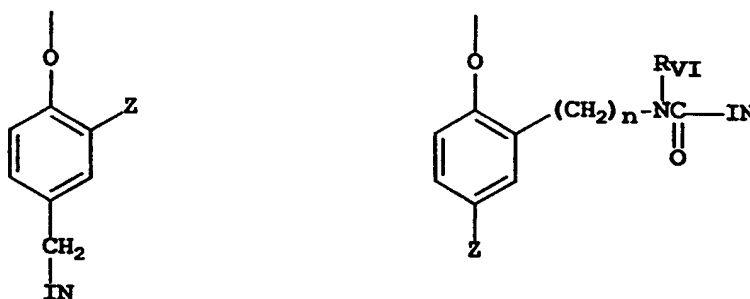
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wherein R_I is selected from the group consisting of straight and branched alkyls of
 from 1 to about 8 carbon atoms, benzyl, phenyl and alkoxy groups and such
 groups containing none, one or more than one such substituent; R_{II} is selected
 from R_I and $-SR_I$; R_{III} is a straight or branched alkyl group of from 1 to about 5
 15 carbon atoms and m is from 1 to 3; and R_{IV} is selected from the group consisting
 of hydrogen, halogens and alkoxy, phenyl and carbonamido groups, $-COOR_V$ and
 $-NHCOOR_V$ wherein R_V is selected from substituted and unsubstituted alkyl and
 aryl groups.

Although it is typical that the coupler moiety included in the developer
 20 inhibitor-releasing coupler forms an image dye corresponding to the layer in
 which it is located, it may also form a different colour as one associated with a
 different film layer. It may also be useful that the coupler moiety included in the
 developer inhibitor-releasing coupler forms colourless products and/or products

that wash out of the photographic material during processing (so-called "universal" couplers).

As mentioned, the developer inhibitor-releasing coupler may include a timing group, which produces the time-delayed release of the inhibitor group, such as groups using an intramolecular nucleophilic substitution reaction (U.S. Patent No. 4,248,962); groups utilising an electron transfer reaction along a conjugated system (U.S. patent Nos. 4,409,323, 4,421,845 and 4,861,701 and Japanese Applications 57-188035; 58-98728; 58-209736; 58-209738); groups utilizing ester hydrolysis (German Patent Application (OLS) No. 2,626,315); groups that function as a coupler or reducing agent after the coupler reaction (U.S. Patent Nos. 4,438,193 and 4,618,571) and groups that combine the features described above. It is typical that the timing group is of one of the formulae:



wherein IN is the inhibitor moiety, Z is selected from the group consisting of nitro, cyano, alkylsulfonyl; sulfamoyl ($-\text{SO}_2\text{NR}_2$) and sulfonamido ($-\text{NR}\text{SO}_2\text{R}$) groups; n is 0 or 1; and RVI is selected from the group consisting of substituted and unsubstituted alkyl and phenyl groups. The oxygen atom of each timing group is bonded to the coupling-off position of the respective coupler moiety of the DIAR.

The timing or linking groups may also function by electron transfer down an unconjugated chain. Linking groups are known in the art under various names. Often they have been referred to as groups capable of utilising a hemiacetal or iminoketal cleavage reaction or as groups capable of utilising a cleavage reaction due to ester hydrolysis such as U.S. 4,546,073. This electron transfer down an unconjugated chain typically results in a relatively fast decomposition and the

production of carbon dioxide, formaldehyde or other low molecular weight by-products. The groups are exemplified in EP 464,612, EP 523,451, U.S. 4,146,396, Japanese Kokai 60-249148 and 60-249149.

It is also contemplated that the concepts of the present invention may be employed to obtain reflection colour prints as described in Research Disclosure, November 1979, Item 18716, available from Kenneth Mason Publications, Ltd, Dudley Annex, 12a North Street, Emsworth, Hampshire P0101 7DQ, England, incorporated herein by reference. Materials of the invention may be coated on pH adjusted support as described in U.S. Patent No. 4,917,994; on a support with reduced oxygen permeability (EP 553,339); with epoxy solvents (EP 64,961); with nickel complex stabilisers (U.S. Patent Nos. 4,346,165, 4,540,653 and 4,906,559 for example); with ballasted chelating agents such as those in U.S. Patent No. 4,994,359 to reduce sensitivity to polyvalent cations such as calcium and with stain reducing compounds such as described in U.S. Patent No. 5,068,171. Other compounds useful in combination with the invention are disclosed in Japanese Published Applications described in Derwent Abstracts having accession numbers as follows: 90-072,629, 90-072,630; 90-072,631; 90-072,632; 90-072,633; 90-072,634; 90-077,822; 90-078,229; 90-078,230; 90-079,336; 90-079,337; 90-079,338; 90-079,690; 90-079,691; 90-080,487; 90-080,488; 90-080,489; 90-080,490; 90-080,491; 90-080,492; 90-080,494; 90-085,928; 90-086,669; 90-086,670; 90-087,360; 90-087,361; 90-087,362; 90-087,363; 90-087,364; 90-088,097; 90-093,662; 90-093,663; 90-093,664; 90-093,665; 90-093,666; 90-093,668; 90-094,055; 90-094,056; 90-103,409; 83-62,586 and 83-09,959.

Any silver halide combination can be used for the photographic element, such as silver chloride, silver chlorobromide, silver chlorobromiodide, silver bromide, silver bromiodide, or silver chloriodide. In cases where the emulsion composition is a mixed halide, the minor component may be added in the crystal formation or after formation as part of the sensitisation or melting. The shape of the silver halide emulsion grain can be cubic, pseudo-cubic, octahedral, tetradecahedral or tabular. The emulsions may be precipitated in any suitable

environment such as a ripening environment, a reducing environment or an oxidising environment.

Photographic elements can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image and can then be processed to form a visible dye image. Processing to form a visible dye image includes the step of contacting the element with a colour developing agent to reduce developable silver halide and oxidise the colour developing agent. Oxidised colour developing agent in turn reacts with the coupler to yield a dye.

With negative-working silver halide, the processing step described above provides a negative image. The described elements can be processed in the known Kodak C-41™ colour process as described in The British Journal of Photography Annual of 1988, pp 191-198. Where applicable, the element may be processed in accordance with colour print processes such as the RA-4™ process of Eastman Kodak Company as described in the British Journal of Photography Annual of 1988, pp 198-199. Such negative working emulsions are typically sold with instructions to process using a colour negative method such as the C-41™ or RA-4™ process. To provide a positive (or reversal) image, the colour development step can be preceded by development with a non-chromogenic developing agent to develop exposed silver halide, but not form dye, and followed by uniformly fogging the element to render unexposed silver halide developable. Such reversal emulsions are typically sold with instructions to process using a colour reversal process such as E-6™. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

The multicolour photographic elements of the invention may be processed alternatively in a developer solution that will provide reduce processing times of one minute or less (dry to dry), and particularly reduced colour development times of less than about 25 seconds, such that all colour records are fully developed with aim sensitometry.

Preferred colour developing agents are p-phenylenediamines such as:
4-amino-N,N-diethylaniline hydrochloride,
4-amino-3-methyl-N,N-diethylaniline hydrochloride,

4-amino-3-methyl-N-ethyl-N-(2-methanesulfonamidoethyl)aniline
sesquisulfate hydrate,

4-amino-3-methyl-N-ethyl-N-(2-hydroxyethyl)aniline sulfate,

4-amino-3-(2-methanesulfonamido-ethyl)-N,N-diethylaniline

5 hydrochloride and

4-amino-N-ethyl-N-(2-methoxyethyl)-m-toluidine di-p-toluene sulfonic
acid.

Development is usually followed by the conventional steps of bleaching,
fixing or bleach-fixing, to remove silver or silver halide, washing and drying.

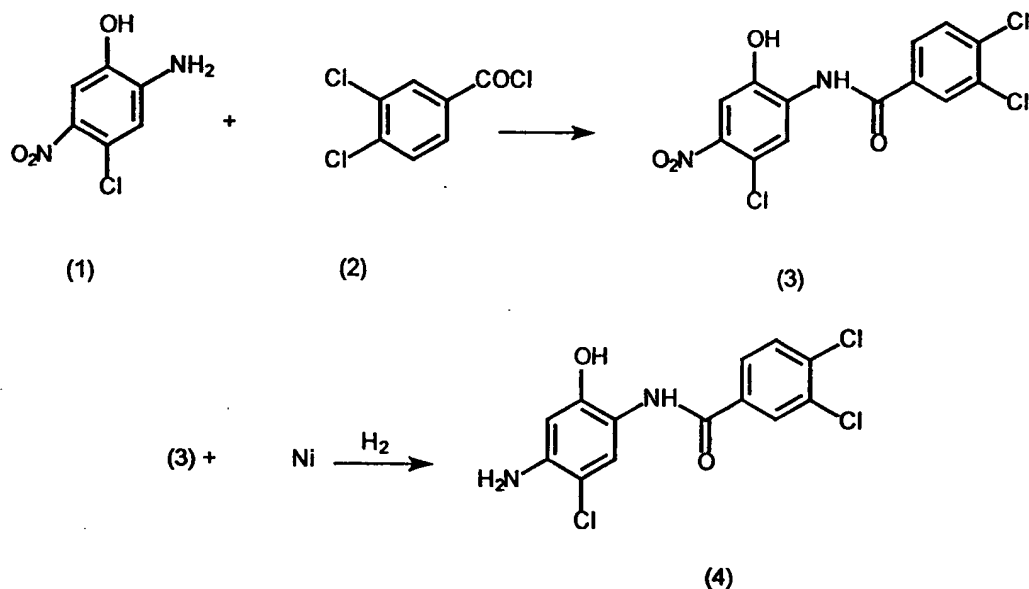
10 The coupler dispersions may be coated with emulsions to form
photographic elements at very low levels of silver (less than 100 mg/m^2). Reasons
for doing this include reducing cost, reducing the thickness of silver halide
emulsion layers to gain sharpness advantages and reducing the environmental
impact during and after processing.

15 One class of low silver photographic material is colour material intended
for redox amplification processes wherein the developed silver acts as a catalyst to
the formation of the dye image. This process can take place in a low volume thin
processor, such as a low volume thin tank (LVTT), for example, as disclosed in
U.S. Patent No. 5,436,118. Redox amplification processes have been described
20 for example in GB 1,268,126, GB 1,399,481, GB 1,403,418, GB 1,560,572, U.S.
Patent Nos. 3,748,138, 3,822,129 and 4,097,278. In such processes, colour
materials are developed to produce a silver image (which may contain only small
amounts of silver) and are then treated with a redox amplifying solution (or a
combined developer-amplifier) to form a dye image.

25 The following examples illustrate the invention but are not to be construed
as to be limiting of the scope thereof. The preparative example is typical of the
synthesis of any of the couplers, which can be prepared analogously by
appropriate selection of reactants.

EXAMPLES**Preparative examples****Synthesis of a coupler of formula (I) (I-1)****A. Preparation of 2-(3,4-Dichlorobenzamido)-4-chloro-5-aminophenol (4)**

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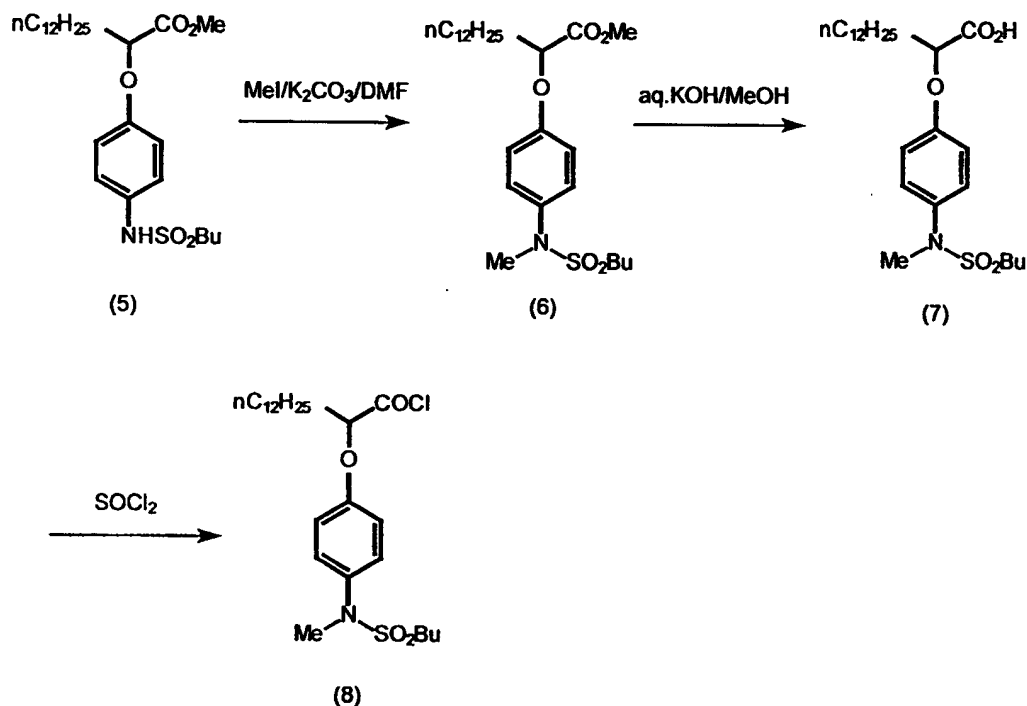
**2-(3,4-dichlorobenzamido)-4-chloro-5-nitrophenol (3).**

3,4-dichlorobenzoyl chloride (2) (38.0g, 0.18mol) was added to a stirred
 10 slurry of 2-amino-4-chloro-5-nitrophenol (1) (34.0g, 0.18mol) in ethyl acetate
 (250ml) and the mixture refluxed for 2 h. After cooling the precipitate was
 filtered and then slurried in hot ethyl acetate (200ml) and filtered again to give
 50g (77%) 2-(3,4-dichlorobenzamido)-4-chloro-5-nitrophenol (3).

2-(3,4-Dichlorobenzamido)-4-chloro-5-aminophenol (4)

The nitrophenol (3) (36.0g, 0.1mol) was dissolved in ethyl acetate (250ml)
 and dimethylformamide (DMF) (50ml). The solution was hydrogenated over
 Raney Nickel at 3040kPa (30atm)/25C for 15 h. The catalyst was removed by
 filtration through a pad of Kieselguhr and the ethyl acetate removed *in vacuo*.
 20 The residual solution of aminophenol (4) in DMF was poured on to an ice/water
 mixture (1.5l) to precipitate aminophenol (4) (27g, yield 84%), which was
 collected by filtration and dried. This was stored under a blanket of nitrogen
 while the ballast acid chloride was prepared.

B. Preparation of 2-(4-N-Methyl-N-butanesulphonamido)phenoxy-tetradecanoyl chloride (8)



5

Methyl 2-(4-N-methyl-N-butanesulfonamido)phenoxytetradecanoate (6)

A solution in DMF (200ml) of the ballast ester (5) (50.0g, 0.1mol),
 10 prepared as described in US Patent 5,972,587, was stirred at room temperature
 with solid potassium carbonate (27.6g, 0.2mol) while a solution of iodomethane
 (42.6g, 0.3mol) in DMF (50ml) was dripped in over 0.5 h. When addition was
 complete, the reaction mixture was heated on a steam bath for 1 h then cooled and
 solvent removed under reduced pressure. The residue was partitioned between
 15 ethyl acetate and dilute hydrochloric acid (300ml each) and the organic phase
 separated and dried over magnesium sulfate. Removal of ethyl acetate gave the
 crude product as a yellow oil which was purified by silica gel column
 chromatography (4:1 v/v 60-80 petrol/ethyl acetate) to give (6) as a colourless oil
 which rapidly solidified to a white solid on standing, 43.5g (85%).

20 HPLC gave 100% purity for (6) whose correct structure was confirmed by
 nmr and mass spectra.

2-(4-N-Methyl-N-butanesulfonamido)phenoxytetradecanoic acid (7)

The ester (6) (56.0g, 0.12mol) was taken up in a mixture of methanol (300ml) and tetrahydrofuran (THF) (50ml). A solution of excess potassium hydroxide (19.5g, 0.36mol) in water (50ml) was added in one charge and the
5 solution stirred at room temperature for 1.5 h. The solvent was removed to about 1/3 original volume and the residue carefully poured onto a well stirred mixture of ice-water (2 l) containing concentrated hydrochloric acid (50ml). Product acid (7) was obtained as a white solid after filtration and oven drying, 56.0g (quantitative).

The structure of (7) was confirmed by ir, nmr and mass spectra.

10

2-(4-N-Methyl-N-butanesulphonamido)phenoxytetradecanoyl chloride (8)

The ballast acid (7) (33.0g, 0.07mol) was refluxed in excess thionyl chloride (150ml) for 0.5 h. After cooling, the solution was evaporated to dryness and dichloromethane (150ml) added followed by further evaporation to give the
15 acid chloride (8) as a brown oil (~35g, assumed quantitative).

The crude acid chloride was used immediately and without further purification for the synthesis of Coupler I-1.

C. Preparation of Coupler I-1

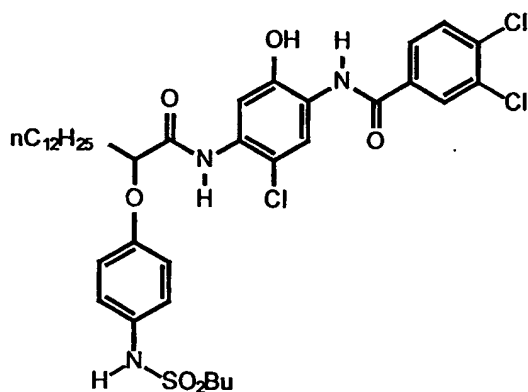
20 2-(3,4-Dichlorobenzamido)-4-chloro-5-aminophenol (3) (20.0g, 0.06mol) was stirred in a mixture of DMF (50ml) and tetrahydrofuran (THF) (150ml) while N,N-dimethylaniline (20ml) was added. The freshly prepared ballast acid chloride (8) (35g, 0.07mol) in THF (50ml) was then added dropwise and the
25 solution stirred at ambient temperature for 2 h. The solvent was removed *in vacuo* and the residue taken up in ethyl acetate (300ml). The organic solution was washed successively with dilute hydrochloric acid and water then separated and dried over magnesium sulfate. Removal of solvent gave the crude coupler which was recrystallised (x3) from acetonitrile to give a I-1 as a clean white solid, 15.0g, (32%), mp 139-141C.

30 HPLC gave 100% purity for the coupler I-1 whose structure was confirmed by ir, nmr and mass spectra.

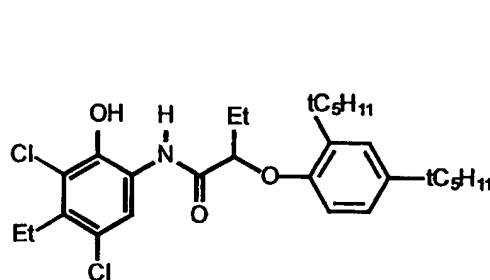
Photographic examples**Dispersion examples**

Inventive couplers I-1 and I-2 were compared with comparison couplers CC-1 and CC-2, having the structures below:-

5



CC-1



CC-2

10 CC-1 was dispersed in gelatin according to the following procedure:-

Coupler CC-1 (5.59g, 6.88mmol) was dissolved in a mixture of p-dodecyl phenol (pDP) (2.8g) and ethyl acetate (2g). The mixture was heated to effect solution. After adding aqueous gelatin (40g, 10%) containing 0.25% di-isopropylnaphthalene sulfonic acid (sodium salt) surfactant at 60C, the mixture was dispersed by ultrasonic agitation for 2 min. using a Dawe Instruments "Soniprobe" and diluted to 50g with water. The completed dispersion was labelled Dispersion 1.

20 Dispersions 2 and 3, incorporating the inventive couplers I-1 and I-2, were prepared in like manner. The same molar quantities of each coupler were used and the weights of pDP permanent coupler solvent were adjusted in proportion to the weight of coupler taken. The schedule is indicated below:-

	Dispersion	Coupler	Coupler Weight	pDP Weight	EtOAc Weight
	1	CC1	5.29g	2.64g	2.0g
	2	I-1	5.38g	2.69g	2.0g
5	3	I-2	5.48g	2.74g	2.0g

A further comparison coupler CC-2 was also dispersed in a similar fashion, except that dibutyl phthalate (dBP) was used as the permanent coupler solvent in place of pDP. For this dispersion, the oil phase component weights were:

Dispersion	Coupler	Coupler Weight	dBP Weight	EtOAc Weight
4	CC2	3.50g	1.75g	2.0g

Each of the above dispersions was further diluted to 300g with an appropriate quantity of aqueous gelatin and mixed with a red-sensitive cubic silver chloride photographic emulsion (average edge length: 0.36 μm) before coating on a resin-coated paper support carrying a precoated gel pad (3g.m^{-2}). A protective gelatin supercoat (1.0g.m^{-2}), containing an appropriate quantity of bis-(vinyl-sulfonylmethyl) ether hardener, was applied over the photosensitive layer. The silver and coupler coverages were, respectively, 0.21g.m^{-2} and 0.831mmol.m^{-2} .

The coating structure is shown below.

25	Gel	1.0 g.m^{-2}	GEL SUPERCOAT
	Hardener*	0.084 g.m^{-2}	
	Coupler	0.831 mM.m^{-2}	PHOTOSENSITIVE LAYER
30	Ag	0.21 g.m^{-2}	
	Gel	1.615 g.m^{-2}	
	Gel	3.0 g.m^{-2}	GEL PAD
35	Resin Coated Paper		

* Hardener = bis(vinylsulphonylmethyl) ether

Sample strips of the coatings were exposed through a step tablet (density range 0 - 3, 0.15 inc.) and developed through standard KODAK RA4™ process solutions. Sensitometric curves were generated for each coating and the spectral absorption characteristics of the image dyes were also measured. The thermal stability of the image dyes was monitored in an accelerated dark keeping test at 75C, 50%RH, while image dye light stability was assessed using standard simulated daylight fading equipment incorporating a Xenon arc source, delivering an exposure intensity of 50Klux at the sample plane. For the latter tests, sample strips were mounted in the fader under a UV-absorbing filter, comprising Tinuvin™-328 (Ciba-Geigy), dispersed in gelatin and coated on a transparent polyester sheet at a coverage of 1.0 g.m-2. At the end of these tests, the sensitometric curves were re-read and compared with the initial curves. Status "A" red density losses from an initial value of 1.0 were recorded.

The results are reproduced in the TABLE, which shows the yellowing and density loss from 1.0 for each of the stability tests, as well as the maximum developed density and the wavelength of maximum absorption of the image dye. This figure, read from the measured spectral absorption curves of developed patch of density near 1.0, is a convenient representation of the image dye hue.

TABLE
Image Dye Hue and Stability Data

	Coated Dispersion	D _{max}	λ _{max} (nm)	Light Stability* ΔD _{1.0}	Dark Stability† ΔD _{1.0}
	2. (I-1)	2.445	661	-0.27	0.00 (Inv.)
	3. (I-2)	2.359	660	-0.25	-0.03 (Inv.)
30	1. (CC1)	2.241	662	-0.40	-0.03 (Comp.)
	4. (CC2)	2.309	663	-0.32	-0.23 (Comp.)

* 6 wk, 50klux Fade, ΔD_{1.0} = Density loss from 1.0

† 6 wk, 75C, 50%RH, ΔD_{1.0} = Density loss from 1.0

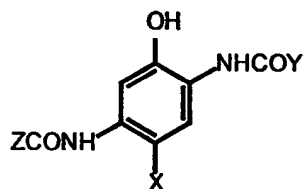
The results show that the couplers I-1 and I-2 of this invention are comparable in activity to the comparison couplers CC1 and CC2, and give dyes with adequately deep hue. The thermal dark stability of the image dye from the comparison coupler CC1 is good, and superior to that of the comparison coupler
5 CC2, but its light stability is poor. The dyes from the inventive couplers I-1 and I-2 retain the excellent dark stability displayed by the analogous dyes from CC1, and also demonstrate good light stability, superior to that of the image dye from CC2 .

Comparison coupler CC2 is already well known as a commercially
10 important component of photographic colour paper products and the image dyes from the inventive couplers are superior to those of CC2 in terms of resistance to decomposition by both light and heat.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations
15 and modifications can be effected within the spirit and scope of the invention.

Claims:

1. A photographic element comprising at least one silver halide emulsion layer having associated therewith a phenolic cyan dye-forming coupler of formula (I)



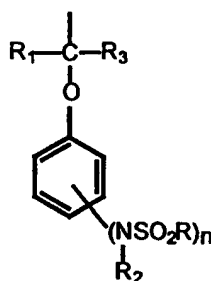
5

(I)

wherein

X is hydrogen or a group that can be split off by the reaction of the coupler with an oxidised colour developing agent, and

10 one of Y and Z is the group



wherein

each R is independently an unsubstituted or substituted alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted;

15

R₁ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

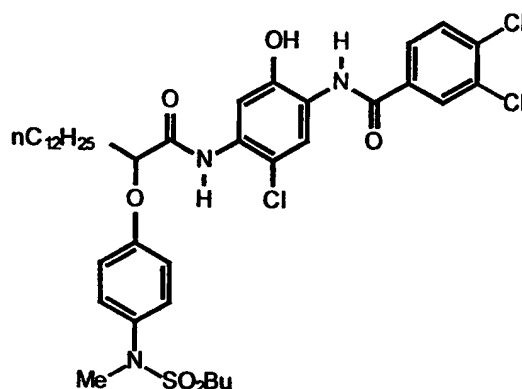
R₂ is an unsubstituted or substituted alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted;

20 R₃ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

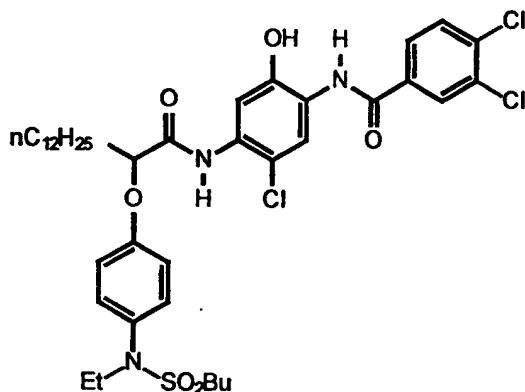
n is 1 or 2, and

the other of Y and Z is an unsubstituted or substituted alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted.

2. An element according to claim 1 wherein R, R₁ and R₂ are independently an unsubstituted or substituted alkyl group.
3. An element according to either of the preceding claims wherein each of R and R₂ is a lower alkyl group.
- 5 4. An element according to any one of the preceding claims wherein R₁ is an alkyl group having at least 8 carbon atoms.
5. An element according to any one of the preceding claims wherein R₃ is hydrogen.
6. An element according to any one of the preceding claims wherein n is 1 and the group -N(R₂)SO₂R is in the para position.
- 10 7. An element according to any one of the preceding claims wherein the group Z contains the N-alkylsulfonamido substituent and the group Y is an unsubstituted or substituted aryl group,
8. An element according to any one of the preceding claims wherein the cyan dye-forming coupler has the structure



9. An element according to any one of claims 1 to 7 wherein the cyan dye-forming coupler has the structure



- 5 10. A multicolour photographic element comprising a support bearing yellow, magenta and cyan image-dye-forming units comprising at least one blue-, green- or red-sensitive silver halide emulsion layer having associated therewith at least one yellow, magenta or cyan dye-forming coupler respectively, wherein the element comprises at least one cyan dye-forming coupler of formula (I) as defined
- 10 in any one of the preceding claims.
11. A process of forming an image in a photographic element after the element has been imagewise exposed to light, comprising contacting the element, as claimed in any one of the preceding claims, with a colour developing agent.
12. A coupler of formula (I) as defined in any one of claims 1 to 9.

INTERNATIONAL SEARCH REPORT

Int. J. Application No

PCT/GB 99/04360

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G03C7/34 C07C311/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03C C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 362 810 A (USAGAWA ET AL) 7 December 1982 (1982-12-07) column 1, line 4 - line 16 column 2, line 5 - line 20 columns 7, 8, table II, coupler 25 column 14, line 9 - line 13 claims 1,2,4	1-3,5,6, 10-12
X	GB 2 070 000 A (KONISHIROKU PHOTO INDUSTRY CO. LTD.) 3 September 1981 (1981-09-03) cited in the application page 1, line 3 - line 9 page 1, line 36 - line 42 page 2, line 42 page 3, coupler 3 page 9, line 33 - line 34 claims 1,4,9,10	1,2,5,7, 10-12
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

18 February 2000

Date of mailing of the international search report

29/02/2000

Name and mailing address of the ISA

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INTERNATIONAL SEARCH REPORT

Int. J. Application No

PCT/GB 99/04360

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>US 4 299 914 A (FUJIMATSU ET AL) 10 November 1981 (1981-11-10) column 1, line 4 - line 9 column 2, line 7 - line 21 columns 5, 6, coupler 18 column 9, line 63 - line 67 claims 1,2,6-9,14,15,20-22</p>	<p>1-5,7, 10-12</p>
X	<p>DATABASE WPI Section Ch, Week 198422 Derwent Publications Ltd., London, GB; Class E24, AN 1984-136665 XP002130870 -& JP 59 069755 A (KONISHIROKU PHOTO IND CO LTD), 20 April 1984 (1984-04-20) abstract page 4, coupler 19</p>	<p>1-5,7, 10-12</p>
A	<p>US 4 124 396 A (OSBORN) 7 November 1978 (1978-11-07) column 1, line 6 - line 14 column 1, line 64 -column 2, line 5 column 7, line 58 -column 8, line 51 claims 1,5,6,10</p>	<p>1-12</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/04360

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		IT 1094169 B	26-07-1985
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		JP 59037821 B	12-09-1984
		US T980004 I	06-03-1979

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference 79888/11527	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/GB 99/ 04360	International filing date (day/month/year) 22/12/1999	(Earliest) Priority Date (day/month/year) 22/12/1998
Applicant EASTMAN KODAK et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the title,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

5. With regard to the **abstract**,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.



None of the figures.

INTERNATIONAL SEARCH REPORT

International Application No

F GB 99/04360

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G03C7/34 C07C311/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G03C C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

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X	US 4 362 810 A (USAGAWA ET AL) 7 December 1982 (1982-12-07) column 1, line 4 - line 16 column 2, line 5 - line 20 columns 7, 8, table II, coupler 25 column 14, line 9 - line 13 claims 1,2,4 ---	1-3,5,6, 10-12
X	GB 2 070 000 A (KONISHIROKU PHOTO INDUSTRY CO. LTD.) 3 September 1981 (1981-09-03) cited in the application page 1, line 3 - line 9 page 1, line 36 - line 42 page 2, line 42 page 3, coupler 3 page 9, line 33 - line 34 claims 1,4,9,10 --- -/--	1,2,5,7, 10-12

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

18 February 2000

Date of mailing of the international search report

29/02/2000

Name and mailing address of the ISA

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Fax: (+31-70) 340-3016

Authorized officer

Binder, R

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INTERNATIONAL SEARCH REPORT

International Application No

GB 99/04360

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	DATABASE WPI Section Ch, Week 198422 Derwent Publications Ltd., London, GB; Class E24, AN 1984-136665 XP002130870 -& JP 59 069755 A (KONISHIROKU PHOTO IND CO LTD), 20 April 1984 (1984-04-20) abstract page 4, coupler 19 ---	1-5,7, 10-12
A	US 4 124 396 A (OSBORN) 7 November 1978 (1978-11-07) column 1, line 6 - line 14 column 1, line 64 -column 2, line 5 column 7, line 58 -column 8, line 51 claims 1,5,6,10 -----	1-12

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

F GB 99/04360

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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GB 2070000 A	03-09-1981	JP 1483856 C	27-02-1989
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		FR 2382437 A	29-09-1978
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		IT 1094169 B	26-07-1985
		JP 1268625 C	10-06-1985
		JP 53109630 A	25-09-1978
		JP 59037821 B	12-09-1984
		US T980004 I	06-03-1979

XP-002130870

AN - 1984-136665 [22]

AP - JP19820180968 19821014; JP19820180968 19821014

CPY - KONS

DC - E24 G06 P83

FS - CPI;GMPi

IC - C07D257/04 ; G03C7/34

MC - E05-G08 E10-A08 E10-A10 E10-A15 E10-A16 E10-D03A E26-A G06-C01 G06-H08A

M3 - [02] C316 F010 F020 F021 F111 F431 G010 G011 G012 G013 G014 G015 G017

G018 G019 G020 G021 G029 G040 G100 G112 G113 G221 H4 H401 H441 H521

H541 H542 H543 H592 H594 H599 H6 H600 H601 H602 H608 H609 H641 H642

H643 H681 H682 H683 H684 H685 H689 H8 J0 J012 J013 J014 J131 J132 J133

J231 J232 J241 J242 J3 J331 J332 J341 J581 J582 J583 K353 K442 K499

L143 L199 M1 M113 M121 M122 M123 M129 M136 M139 M141 M142 M147 M149

M210 M211 M212 M213 M214 M215 M216 M220 M221 M222 M223 M224 M225 M226

M231 M232 M233 M240 M262 M271 M272 M280 M281 M282 M283 M311 M312 M313

M314 M315 M316 M321 M322 M331 M332 M333 M334 M340 M342 M343 M344 M349

M353 M372 M381 M391 M413 M414 M510 M520 M521 M532 M533 M540 M781 M903

Q311 Q345 R043

M4 - [01] C316 F010 F020 F021 F111 F431 G010 G011 G012 G013 G014 G015 G017

G018 G019 G020 G021 G029 G040 G100 G112 G113 G221 H4 H401 H441 H521

H541 H542 H543 H592 H594 H599 H6 H600 H601 H602 H608 H609 H641 H642

H643 H681 H682 H683 H684 H685 H689 H8 J0 J012 J013 J014 J131 J132 J133

J231 J232 J241 J242 J3 J331 J332 J341 J581 J582 J583 K353 K442 K499

K534 L143 L199 M1 M113 M121 M122 M123 M129 M136 M139 M141 M142 M145

M147 M149 M210 M211 M212 M213 M214 M215 M216 M220 M221 M222 M223 M224

M225 M226 M231 M232 M233 M240 M262 M271 M272 M280 M281 M282 M283 M311

M312 M313 M314 M315 M316 M321 M322 M331 M332 M333 M334 M340 M342 M343

M344 M349 M353 M372 M381 M391 M413 M414 M510 M520 M521 M532 M533 M540

M781 M903 Q311 Q345 R043 W003 W030 W111 W120 W122 W123 W131 W335

PA - (KONS) KONISHIROKU PHOTO IND CO LTD

PN - JP59069755 A 19840420 DW198422 010pp

- JP3007100B B 19910131 DW199109 000pp

PR - JP19820180968 19821014

XA - C1984-057759

XIC - C07D-257/04 ; G03C-007/34

XP - N1984-101228

AB - J59069755 Coupler is claimed having benzamido gp. (which is substd. by fluorinated alkyl at o-position) at the 2-position of phenolic nucleus and acylamino gp. at the 5-position.

- Coupler has excellent photographic speed, max. density of produced image dye, and also light fastness, heat resistance and moisture resistance of produced image dye. In addn., it gives rise to little yellow stain.

- Pref. coupler is of formula (I) where Rf is alkyl substd. by at least 1 F (e.g. fluoro-methyl, trifluoromethyl, heptafluoroisopropyl, etc.); R1 is alkyl (e.g. t-butyl, n-octyl, n-dodecyl, n-hexadecyl, etc.) substd. alkyl (e.g. phenethyl, n-hexyloxyethyl, 1-(2,4-di-t-acylphenoxy)propyl, 3-(2,4,6-trichlorophenoxy)dodecyl, 1-(3-butanefluoronylamino phenoxy)nonyl, etc.), or aryl (e.g. phenyl, m-pentadecylphenyl, p-lauroylaminophenyl, naphthyl, etc.); R2 is H, halogen or organic monovalent gp. (e.g. opt. substd. alkyl,

alkylsulphonyl, arylsulphonyl, alkoxycarbonyl, aryloxy, acyl, alkoxy, aryloxy, cyano, carboxyl, alkylsulphonamido, arylsulphonamido, etc.); Z is H or gp. capable of being eliminated by coupling with oxidn. prod. of colour developer (e.g. halogen, alkoxy, aryloxy, heteroxyloxy, alkylthio, arylthio, heteroylthio, alkylsulphonamido, arylsulphonamido, acyl, heteroyl, arylazo, phosphonyloxy, etc.); and n is 1, 2 or 3.(0/0)

IW - PHOTOGRAPH CYAN PHENOLIC COUPLE FLUORINATED ALKYL SUBSTITUTE BENZAMIDO GROUP ACYLAMINO GROUP PHENOLIC NUCLEUS

IKW - PHOTOGRAPH CYAN PHENOLIC COUPLE FLUORINATED ALKYL SUBSTITUTE BENZAMIDO GROUP ACYLAMINO GROUP PHENOLIC NUCLEUS

NC - 001

OPD - 1982-10-14

ORD - 1984-04-20

PAW - (KONS) KONISHIROKU PHOTO IND CO LTD

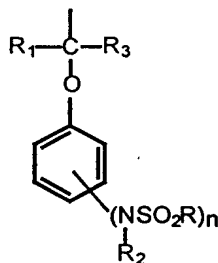
TI - Photographic cyan phenolic coupler - having fluorinated alkyl-substd. benzamido gp. and acylamino gp. on phenolic nucleus

In recent years, a great deal of study has been conducted to improve image couplers for silver halide photosensitive materials in terms of improved colour reproducibility and image dye stability. However, further improvements are needed, particularly in the area of cyan couplers. In general, cyan dyes are formed
5 by the reaction of, generally, phenols or naphthols with oxidised colour developing agents as described, for example, in U.S. Patent Nos. 2,367,351, 2,423,730, 2,474,293, 2,772,161, 2,772,162, 2,895,826, 2,920,961, 3,002,836, 3,034, 892, 3,041,236, 3,466,622, 3,476,563, 3,552,962, 3,758,308, 3,779,763, 3,839,044, 3,880,661, 3,998,642, 4,333,999, 4,883,746, 4,990,436, 4,960,685,
10 5,476,757 and 5,614,357; in French Patent Nos. 1,478,188 and 1,479,043, in UK Patent No. 2,070,000 and "Farbkuppler - Eine Literature Übersicht," published in Agfa Mitteilungen, Band III, pp. 156-175 (1961). Also useful are the cyan couplers described in, for instance, European Patent Application Nos. 544,322; 556,700; 556,777; 565,096; 570,006; and 574,948.

15 These types of image couplers can be used either by being incorporated in the photographic silver halide emulsion layers or externally in the processing baths. In the former case the couplers must have ballast substituents built into the molecule to prevent the couplers from migrating from one layer into another. Although these couplers have been used extensively in colour photographic film
20 and paper products, the dyes derived from them still suffer from poor stability to heat, humidity or light, low coupling efficiency or optical density, and in particular from undesirable blue and green absorptions which cause considerable reduction in colour reproduction and colour saturation.

25 2,5-diacylamino phenols are well known in the art of photography, and it is also well known that image dyes derived from them exhibit good resistance to fading by heat and humidity. However their image dyes are deficient in their ability to withstand the effects of light. Moreover, their absorption bands tend to lie at shorter wavelengths than is desirable, particularly for colour paper applications.

one of Y and Z is the group



wherein

each R is independently an unsubstituted or substituted alkyl or aryl group or a
5 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from
nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted;

R₁ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

R₂ is an unsubstituted or substituted alkyl or aryl group or a 5-10 membered
heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen
10 and sulfur, which ring is unsubstituted or substituted;

R₃ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

n is 1 or 2, and

the other of Y and Z is an unsubstituted or substituted alkyl or aryl group or a
5-10 membered heterocyclic ring which contains one or more heteroatoms selected from
15 nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted.

In another embodiment of the invention there is provided a multicolour
photographic element comprising a support bearing yellow, magenta and cyan image-dye-
forming units comprising at least one blue-, green- or red-sensitive silver halide emulsion
layer having associated therewith at least one yellow, magenta or cyan dye-forming coupler
20 respectively, wherein the element comprises at least one cyan dye-forming coupler of
formula (I) as herein described.

In yet another embodiment of the invention there is provided a process of
forming an image in a photographic element as hereinbefore defined after the
element has been imagewise exposed to light, comprising contacting the element,
25 as herein described, with a colour developing agent.

In a further embodiment of the invention there is provided a novel coupler
of formula (I) as herein described.

Advantageous Effect of the Invention

This invention provides an element which yields a cyan image of good hue, with good stability to heat, humidity and light, whilst retaining the other properties desirable for good photographic performance.

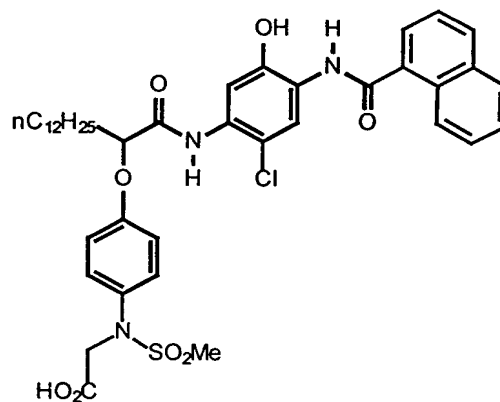
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Detailed Description of the Invention

As used herein and throughout the specification unless where specifically stated otherwise, the term "alkyl" refers to an unsaturated or saturated, straight or branched chain alkyl group, including alkenyl and aralkyl, and includes cyclic alkyl groups, including
10 cycloalkenyl, having 3-8 carbon atoms and the term "aryl" includes specifically fused aryl. The term "lower alkyl" refers to an alkyl group having up to 6 carbon atoms, preferably up to 4 carbon atoms.

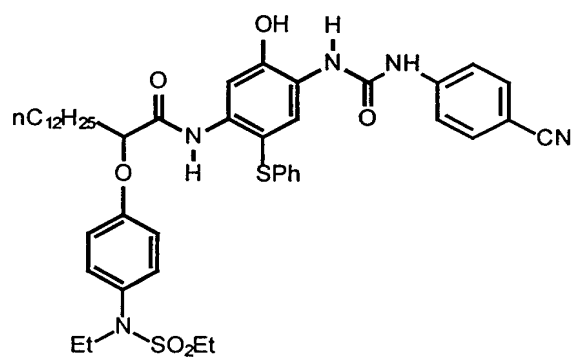
In a preferred embodiment of the invention R, R₁ and R₂ are independently an unsubstituted or substituted alkyl group, with at least one of these normally
15 being a ballast group having at least 8 carbon atoms to render the coupler substantially nondiffusible from the layer in which it is coated. More preferably R and R₂ are lower alkyl groups, especially methyl or ethyl, and the ballast is provided in R₁, which may desirably contain at least 12 carbon atoms. Desirably R₃ is a hydrogen atom. Preferably n is 1 and the -N(R₂)SO₂R group is in the para
20 position although it is possible for there to be one or two such groups in the ortho or meta positions.

Preferably the group Z contains the N-alkylsulfonamido substituent and the group Y is suitably an unsubstituted or substituted aryl group, which may provide a ballast residue, and is especially a phenyl group substituted, for example
25 with one or more chloro, fluoro, trifluoromethyl, cyano, alkoxycarbonyl or alkylsulfonyl groups or it may be a naphthyl, pyridyl or a fluoro-substituted alkyl group.



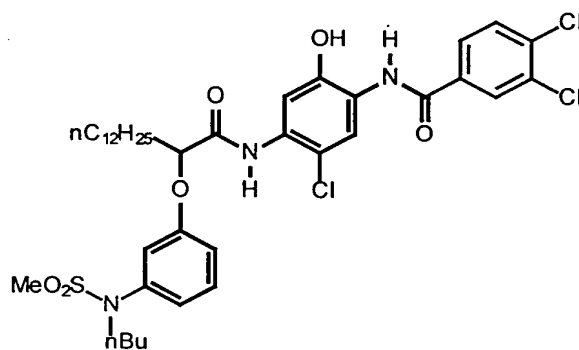
I-9

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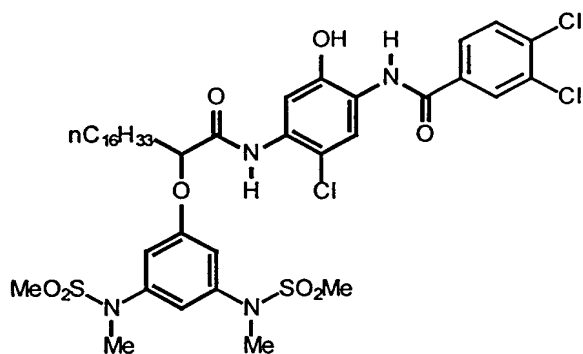
I-10

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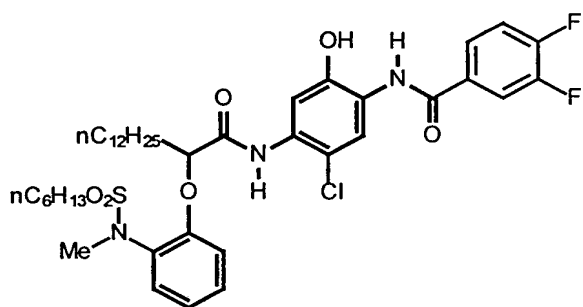


I-11

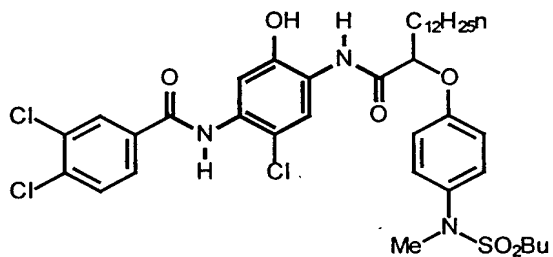
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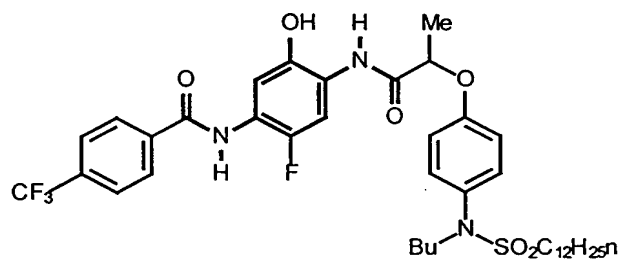
1-12



I-13



1-14



1-15

If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular substituents used may be selected by those skilled in the art to attain the desired photographic properties for a specific application and can include, for example, hydrophobic
5 groups, solubilizing groups, blocking groups, releasing or releasable groups. Generally, the above groups and substituents thereof may include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected.

10 Representative substituents on ballast groups include alkyl, aryl, alkoxy, aryloxy, alkylthio, hydroxy, halogen, alkoxycarbonyl, aryloxy carbonyl, carboxy, acyl, acyloxy, amino, anilino, carbonamido, carbamoyl, alkylsulfonyl, arylsulfonyl, sulfonamido and sulfamoyl groups wherein the substituents typically contain 1 to 42 carbon atoms. Such substituents can also be further substituted.

15 The materials of the invention can be used in any of the ways and in any of the combinations known in the art. Typically, the invention materials are incorporated in a silver halide emulsion and the emulsion coated as a layer on a support to form part of a photographic element. Alternatively, unless provided otherwise, they can be incorporated at a location adjacent to the silver halide
20 emulsion layer where, during development, they will be in reactive association with development products such as oxidised colour developing agent. Thus, as used herein, the term "associated" signifies that the compound is in the silver halide emulsion layer or in an adjacent location where, during processing, it is capable of reacting with silver halide development products.

25 The photographic elements can be single colour elements or multicolour elements. Multicolour elements contain image dye-forming units sensitive to each of the three primary regions of the spectrum. Each unit can comprise a single emulsion layer or multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming
30 units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer.

A typical multicolour photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver
5 halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layers, interlayers, overcoat layers and subbing layers.

10 In the following discussion of suitable materials for use in the emulsions and elements that can be used in conjunction with this photographic element, reference will be made to Research Disclosure, September 1996, Item 38957, published by Kenneth Mason Publications, Ltd., Dudley House, 12 North Street, Emsworth, Hampshire PO10 7DQ, England, which will be identified hereafter by
15 the term "Research Disclosure." The contents of the Research Disclosure, including the patents and publications referenced therein, are incorporated herein by reference, and the Sections hereafter referred to are Sections of the Research Disclosure.

The emulsions can be surface-sensitive emulsions, i.e. emulsions that form
20 latent images primarily on the surfaces of the silver halide grains, or the emulsions can form internal latent images predominantly in the interior of the silver halide grains. The emulsions can be negative-working emulsions, such as surface-sensitive emulsions or unfogged internal latent image-forming emulsions, or direct-positive emulsions of the unfogged, internal latent image-forming type,
25 which are positive-working when development is conducted with uniform light exposure or in the presence of a nucleating agent.

Suitable emulsions and their preparation as well as methods of chemical and spectral sensitisation are described in Sections I and III-IV. Vehicles and vehicle related addenda are described in Section II. Dye image formers and
30 modifiers are described in Section X. Various additives such as UV dyes, brighteners, luminescent dyes, antifoggants, stabilizers, light absorbing and scattering materials, coating aids, plasticizers, lubricants, antistats and matting

The invention may be practised with any permanent high-boiling solvent known to be useful in the art, such as an aryl ester, such as dibutyl phthalate, diundecyl phthalate; phenols, such as p-dodecyl phenol, 2,4-di-isoamyl phenol: phosphates, such as trihexyl phosphate and tricresyl phosphate; alcohols, such as
5 oleyl alcohol and hexadecanol and amides such as diethyldodecanamide and dibutylacetanilide.

The resulting organic solution may then be mixed with an aqueous gelatin solution and the mixture passed through a mechanical mixing device suitable for high-shear or turbulent mixing generally suitable for preparing photographic
10 emulsified dispersions, such as a colloid mill, homogenizer, microfluidizer, high-speed mixer, ultrasonic dispersing apparatus, blade mixer, device in which a liquid stream is pumped at high pressure through an orifice or interaction chamber, Gaulin mill or blender to form small particles of the organic phase suspended in the aqueous phase. More than one type of device may be used to prepare the
15 dispersions. The auxiliary organic solvent may then removed by evaporation, noodle washing, or membrane dialysis. The dispersion particles preferably have an average particle size of less than $2\mu\text{m}$, generally from about 0.02 to $2\mu\text{m}$, more preferably from about 0.02 to $0.5\mu\text{m}$, especially from about 0.02 to $0.3\mu\text{m}$. These methods are described in detail in U.S. Patent Nos. 2,322,027, 2,787,544,
20 2,801,170, 2,801,171, 2,949,360 and 3,396,027, the disclosures of which are incorporated by reference herein.

Examples of suitable auxiliary solvents which can be used in the present invention include: ethyl acetate, isopropyl acetate, butyl acetate, ethyl propionate, 2-ethoxyethylacetate, 2-(2-butoxyethoxy) ethyl acetate, dimethylformamide,
25 2-methyl tetrahydrofuran, triethyl-phosphate, cyclohexanone, butoxyethyl acetate, methyl isobutyl ketone, methyl acetate, 4-methyl-2-pentanol, diethyl carbitol, 1,1,2-trichloroethane and 1,2-di-chloropropane.

The aqueous phase of the coupler dispersions for use in the invention preferably comprises gelatin as a hydrophilic colloid. This may be gelatin or a
30 modified gelatin such as acetylated gelatin, phthalated gelatin or oxidized gelatin. Gelatin may be base-processed, such as lime-processed gelatin, or may be acid-processed, such as acid-processed ossein gelatin. Other hydrophilic colloids may also

The materials for use in the invention may also be used in combination with filter dye layers comprising colloidal silver sol or yellow, cyan and/or magenta filter dyes, either as oil-in-water dispersions, latex dispersions or as solid particle dispersions. Additionally, they may be used with "smearing" couplers (e.g. as described in U.S. Patent Nos. 4,366,237, 4,420,556, 4,543,323 and in EP 96,570) Also, the compositions may be blocked or coated in protected form as described, for example, in Japanese Application 61/258,249 or U.S. Patent No. 5,019,492.

The invention materials may further be used in combination with image-modifying compounds such as "Developer Inhibitor-Releasing" compounds (DIRs). DIRs useful in conjunction with the compositions of the invention are known in the art and examples are described in U.S. Patent Nos. 3,137,578; 3,148,022; 3,148,062; 3,227,554; 3,384,657; 3,379,529; 3,615,506; 3,617,291; 3,620,746; 3,701,783; 3,733,201; 4,049,455; 4,095,984; 4,126,459; 4,149,886; 4,150,228; 4,211,562; 4,248,962; 4,259,437; 4,362,878; 4,409,323; 4,477,563; 4,782,012; 4,962,018; 4,500,634; 4,579,816; 4,607,004; 4,618,571; 4,678,739; 4,746,600; 4,746,601; 4,791,049; 4,857,447; 4,865,959; 4,880,342; 4,886,736; 4,937,179; 4,946,767; 4,948,716; 4,952,485; 4,956,269; 4,959,299; 4,966,835; 4,985,336 as well as in patent publications GB 1,560,240; GB 2,007,662; GB 2,032,914; GB 2,099,167; DE 2,842,063; DE 2,937,127; DE 3,636,824; DE 3,644,416 as well as the following European Patent Publications: 272,573; 335,319; 336,411; 346, 899; 362, 870; 365,252; 365,346; 373,382; 376,212; 377,463; 378,236; 384,670; 396,486; 401,612; 401,613.

Such compounds are also disclosed in "Developer-Inhibitor-Releasing (DIR) Couplers for Color Photography," C.R. Barr, J.R. Thirtle and P.W. Vittum in Photographic Science and Engineering, Vol.13, p.174 (1969), incorporated herein by reference. Generally, the developer inhibitor-releasing (DIR) couplers include a coupler moiety and an inhibitor coupling-off moiety (IN). The inhibitor-releasing couplers may be of the time-delayed type (DIAR couplers) which also include a timing moiety or chemical switch which produces a delayed release of inhibitor. Examples of typical inhibitor moieties are: oxazoles, thiazoles, diazoles, triazoles, oxadiazoles, thiadiazoles, oxathiazoles, thiatriazoles,

production of carbon dioxide, formaldehyde or other low molecular weight by-products. The groups are exemplified in EP 464,612, EP 523,451, U.S. 4,146,396, Japanese Kokai 60-249148 and 60-249149.

It is also contemplated that the concepts of the present invention may be employed to obtain reflection colour prints as described in Research Disclosure, November 1979, Item 18716, available from Kenneth Mason Publications, Ltd, Dudley Annex, 12a North Street, Emsworth, Hampshire P0101 7DQ, England, incorporated herein by reference. Materials of the invention may be coated on pH adjusted support as described in U.S. Patent No. 4,917,994; on a support with reduced oxygen permeability (EP 553,339); with epoxy solvents (EP 64,961); with nickel complex stabilisers (U.S. Patent Nos. 4,346,165, 4,540,653 and 4,906,559 for example); with ballasted chelating agents such as those in U.S. Patent No. 4,994,359 to reduce sensitivity to polyvalent cations such as calcium and with stain reducing compounds such as described in U.S. Patent No. 5,068,171. Other compounds useful in combination with the invention are disclosed in Japanese Published Applications described in Derwent Abstracts having accession numbers as follows: 90-072,629, 90-072,630; 90-072,631; 90-072,632; 90-072,633; 90-072,634; 90-077,822; 90-078,229; 90-078,230; 90-079,336; 90-079,337; 90-079,338; 90-079,690; 90-079,691; 90-080,487; 90-080,488; 90-080,489; 90-080,490; 90-080,491; 90-080,492; 90-080,494; 90-085,928; 90-086,669; 90-086,670; 90-087,360; 90-087,361; 90-087,362; 90-087,363; 90-087,364; 90-088,097; 90-093,662; 90-093,663; 90-093,664; 90-093,665; 90-093,666; 90-093,668; 90-094,055; 90-094,056; 90-103,409; 83-62,586 and 83-09,959.

Any silver halide combination can be used for the photographic element, such as silver chloride, silver chlorobromide, silver chlorobromiodide, silver bromide, silver bromiodide, or silver chloriodide. In cases where the emulsion composition is a mixed halide, the minor component may be added in the crystal formation or after formation as part of the sensitisation or melting. The shape of the silver halide emulsion grain can be cubic, pseudo-cubic, octahedral, tetradecahedral or tabular. The emulsions may be precipitated in any suitable

The results show that the couplers I-1 and I-2 of this invention are comparable in activity to the comparison couplers CC1 and CC2, and give dyes with adequately deep hue. The thermal dark stability of the image dye from the comparison coupler CC1 is good, and superior to that of the comparison coupler
5 CC2, but its light stability is poor. The dyes from the inventive couplers I-1 and I-2 retain the excellent dark stability displayed by the analogous dyes from CC1, and also demonstrate good light stability, superior to that of the image dye from CC2 .

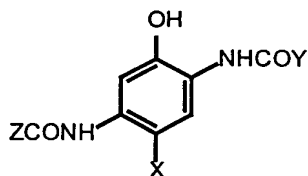
Comparison coupler CC2 is already well known as a commercially
10 important component of photographic colour paper products and the image dyes from the inventive couplers are superior to those of CC2 in terms of resistance to decomposition by both light and heat.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations
15 and modifications can be effected within the spirit and scope of the invention.

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Claims:

1. A photographic element comprising at least one silver halide emulsion layer having associated therewith a phenolic cyan dye-forming coupler of formula (I)

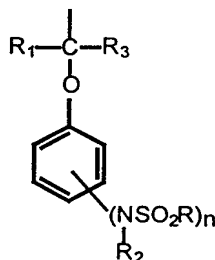


(I)

wherein

X is hydrogen or a group that can be split off by the reaction of the coupler with an oxidised colour developing agent, and

one of Y and Z is the group



wherein

each R is independently an unsubstituted or substituted alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted;

R₁ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

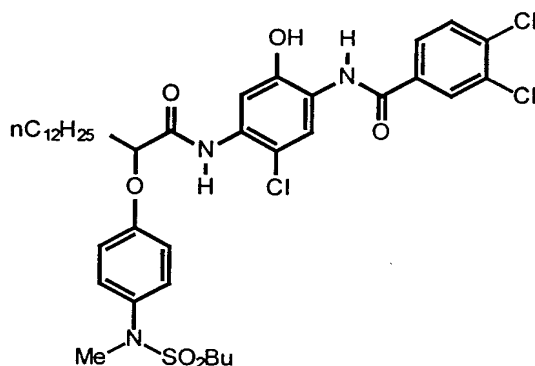
R₂ is an unsubstituted or substituted alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted;

R₃ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

n is 1 or 2, and

the other of Y and Z is an unsubstituted or substituted alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted.

2. An element according to claim 1 wherein R, R₁ and R₂ are independently an unsubstituted or substituted alkyl group.
3. An element according to either of the preceding claims wherein each of R and R₂ is a lower alkyl group.
- 5 4. An element according to any one of the preceding claims wherein R₁ is an alkyl group having at least 8 carbon atoms.
5. An element according to any one of the preceding claims wherein R₃ is hydrogen.
6. An element according to any one of the preceding claims wherein n is 1 and the group -N(R₂)SO₂R is in the para position.
- 10 7. An element according to any one of the preceding claims wherein the group Z contains the N-alkylsulfonamido substituent and the group Y is an unsubstituted or substituted aryl group,
8. An element according to any one of the preceding claims wherein the cyan dye-forming coupler has the structure



15

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

HAILE, Helen C. et al
KODAK LIMITED
Patent Department
Headstone Drive
HARROW, MIDDLESEX HA1 4TY
GRANDE BRETAGNE

PCT

NOTIFICATION OF TRANSMITTAL OF THE INTERNATIONAL PRELIMINARY EXAMINATION REPORT (PCT Rule 71.1)

Date of mailing (day/month/year)	23.03.2001
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Applicant's or agent's file reference 79888/11527	IMPORTANT NOTIFICATION
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International application No. PCT/GB99/04360	International filing date (day/month/year) 22/12/1999	Priority date (day/month/year) 22/12/1998
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Applicant EASTMAN KODAK et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/	Authorized officer
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 79888/11527		FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB99/04360	International filing date (day/month/year) 22/12/1999	Priority date (day/month/year) 22/12/1998	
International Patent Classification (IPC) or national classification and IPC G03C7/34			
Applicant EASTMAN KODAK et al.			

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 4 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 13 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 30/06/2000	Date of completion of this report 23.03.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Binder, R Telephone No. +49 89 2399 8951 

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB99/04360

I. Basis of the report

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).*):

Description, pages:

✓✓✓✓✓
1,3,6-10,13-15,18, as originally filed
19,21,23,24,
26-33

✓✓✓✓✓✓✓✓
2,4,5,11,12,16,17, as received on 03/11/2000 with letter of 02/11/2000
20,22,25,34

Claims, No.:

✓
9-12/ as originally filed

✓
1-8 as received on 03/11/2000 with letter of 02/11/2000

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
☐ the language of publication of the international application (under Rule 48.3(b)).
☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
☐ filed together with the international application in computer readable form.
☐ furnished subsequently to this Authority in written form.
☐ furnished subsequently to this Authority in computer readable form.
☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB99/04360

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-12
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-12
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-12
	No:	Claims	

2. Citations and explanations
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/04360

**CONCERNING SECTION V (CITATIONS AND EXPLANATIONS SUPPORTING THE
STATEMENT WITH REGARD TO NOVELTY, INVENTIVE STEP OR INDUSTRIAL
APPLICABILITY):**

1. None of the available documents describes an element comprising all features of Claims 1 or 10, a process of forming an image comprising all features of Claim 11 or a coupler comprising all features of Claim 12 of the present application or provides a general disclosure that would inevitably lead to such an element, process or coupler. The subject-matter of independent Claims 1 and 10 thus meets the requirements of Article 33 (2) PCT.
2. The closest state of the art is Document 1 (US-A-4362810). With the exception of compound 25, which no longer satisfies formula (I) of Claim 1 of the present application, there is no hint that sulfonamides having an alkyl, aryl or heterocyclic ring attached to the nitrogen may provide advantageous effects. Document 1 rather suggests the use of sulfonamides lacking a substituent on the nitrogen. The subject-matter of independent Claims 1, 10, 11 and 12 thus also meets the requirements of Article 33 (3) PCT.
3. The dependent Claims 2 to 9 describe advantageous embodiments of the elements of Claim 1 and thus likewise meet the requirements of Articles 33 (2) and (3) PCT.

**CONCERNING SECTION VIII (CERTAIN OBSERVATIONS ON THE INTERNATIONAL
APPLICATION):**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claim 10 comprises all the features of Claim 1 but is not appropriately formulated as a claim dependent on the latter (Rule 6.4 PCT). The applicant has indicated that he wishes to retain this claim in its present format.

- 2 -

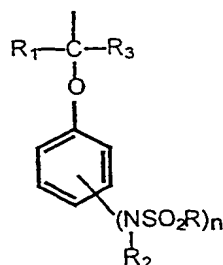
In recent years, a great deal of study has been conducted to improve image couplers for silver halide photosensitive materials in terms of improved colour reproducibility and image dye stability. However, further improvements are needed, particularly in the area of cyan couplers. In general, cyan dyes are formed
5 by the reaction of, generally, phenols or naphthols with oxidised colour developing agents as described, for example, in U.S. Patent Nos. 2,367,351, 2,423,730, 2,474,293, 2,772,161, 2,772,162, 2,895,826, 2,920,961, 3,002,836, 3,034, 892, 3,041,236, 3,466,622, 3,476,563, 3,552,962, 3,758,308, 3,779,763, 3,839,044, 3,880,661, 3,998,642, 4,214,396, 4,299,914, 4,362,810, 4,333,999,
10 4,883,746, 4,990,436, 4,960,685, 5,476,757 and 5,614,357; in French Patent Nos. 1,478,188 and 1,479,043, in UK Patent No. 2,070,000 and "Farbkuppler - Eine Literature Übersicht," published in Agfa Mitteilungen, Band III, pp. 156-175 (1961). Also useful are the cyan couplers described in, for instance, European Patent Application Nos. 544,322; 556,700; 556,777; 565,096; 570,006; and
15 574,948 and JP-A-59069755.

These types of image couplers can be used either by being incorporated in the photographic silver halide emulsion layers or externally in the processing baths. In the former case the couplers must have ballast substituents built into the molecule to prevent the couplers from migrating from one layer into another.
20 Although these couplers have been used extensively in colour photographic film and paper products, the dyes derived from them still suffer from poor stability to heat, humidity or light, low coupling efficiency or optical density, and in particular from undesirable blue and green absorptions which cause considerable reduction in colour reproduction and colour saturation.

25 2,5-diacylamino phenols are well known in the art of photography, and it is also well known that image dyes derived from them exhibit good resistance to fading by heat and humidity. However their image dyes are deficient in their ability to withstand the effects of light. Moreover, their absorption bands tend to lie at shorter wavelengths than is desirable, particularly for colour paper
30 applications.

- 4 -

one of Y and Z is the group



wherein

each R is independently an unsubstituted or substituted alkyl or aryl group or a
 5 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from
 nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted;

R₁ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

R₂ is an unsubstituted or substituted alkyl or aryl group or a 5-10 membered
 heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen
 10 and sulfur, which ring is unsubstituted or substituted;

R₃ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

n is 1 or 2, and each group -N(R₂)SO₂R is in the ortho or para position,

the other of Y and Z is a fluoro-substituted alkyl group or an unsubstituted or
 substituted aryl group or a 5-10 membered heterocyclic ring which contains one or more
 15 heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or
 substituted, provided that (a) when R₂ is an unsubstituted benzyl group, n is 1 and
 -N(R₂)SO₂R is in the ortho position, R may not be a pyridyl group, and (b) at least one of
 R, R₁, R₂, X and Y or Z is or includes a ballast group.

In another embodiment of the invention there is provided a multicolour
 20 photographic element comprising a support bearing yellow, magenta and cyan image-dye-
 forming units comprising at least one blue-, green- or red-sensitive silver halide emulsion
 layer having associated therewith at least one yellow, magenta or cyan dye-forming coupler
 respectively, wherein the element comprises at least one cyan dye-forming coupler of
 formula (I) as herein described.

25 In yet another embodiment of the invention there is provided a process of
 forming an image in a photographic element as hereinbefore defined after the

- 5 -

element has been imagewise exposed to light, comprising contacting the element, as herein described, with a colour developing agent.

In a further embodiment of the invention there is provided a novel coupler of formula (I) as herein described.

5

Advantageous Effect of the Invention

This invention provides an element which yields a cyan image of good hue, with good stability to heat, humidity and light, whilst retaining the other properties desirable for good photographic performance.

10

Detailed Description of the Invention

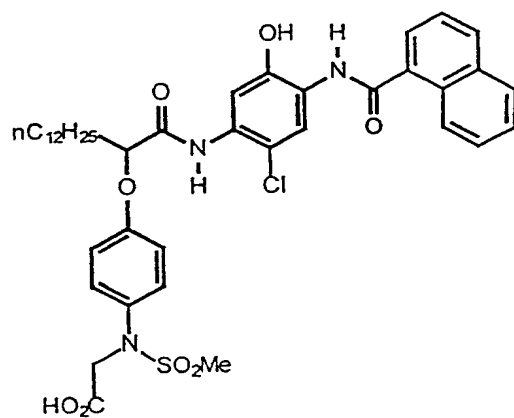
As used herein and throughout the specification unless where specifically stated otherwise, the term "alkyl" refers to an unsaturated or saturated, straight or branched chain alkyl group, including alkenyl and aralkyl, and includes cyclic alkyl groups, including cycloalkenyl, having 3-8 carbon atoms and the term "aryl" includes specifically fused aryl. The term "lower alkyl" refers to an alkyl group having up to 6 carbon atoms, preferably up to 4 carbon atoms.

In a preferred embodiment of the invention R, R₁ and R₂ are independently an unsubstituted or substituted alkyl group, with at least one of these normally being a ballast group having at least 8 carbon atoms to render the coupler substantially nondiffusible from the layer in which it is coated. More preferably R and R₂ are lower alkyl groups, especially methyl or ethyl, and the ballast is provided in R₁, which may desirably contain at least 12 carbon atoms. Desirably R₃ is a hydrogen atom. Preferably n is 1 and the -N(R₂)SO₂R group is in the para position although it is possible for there to be one or two such groups in the ortho positions.

Preferably the group Z contains the -N(R₂SO₂R) substituent and the group Y is suitably an unsubstituted or substituted aryl group, which may provide a ballast residue, and is especially a phenyl group substituted, for example with one or more chloro, fluoro, trifluoromethyl, cyano, alkoxycarbonyl or alkylsulfonyl groups or it may be a naphthyl, pyridyl or a fluoro-substituted alkyl group.

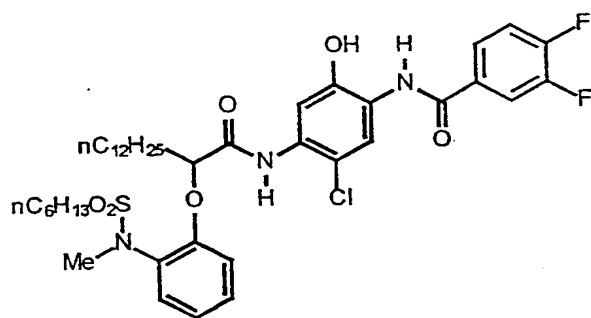
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- 11 -



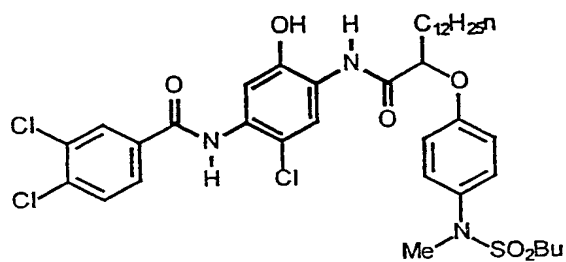
I-9

- 12 -



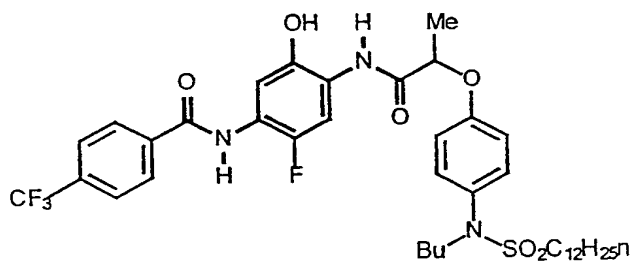
I-13

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1-14

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1-15

- 16 -

If desired, the substituents may themselves be further substituted one or more times with the described substituent groups. The particular substituents used may be selected by those skilled in the art to attain the desired photographic properties for a specific application and can include, for example, hydrophobic groups, solubilizing groups, blocking groups, releasing or releasable groups. Generally, the above groups and substituents thereof may include those having up to 48 carbon atoms, typically 1 to 36 carbon atoms and usually less than 24 carbon atoms, but greater numbers are possible depending on the particular substituents selected.

Representative substituents on ballast groups include alkyl, aryl, alkoxy, aryloxy, alkylthio, hydroxy, halogen, alkoxycarbonyl, aryloxy carbonyl, carboxy, acyl, acyloxy, amino, anilino, carbonamido, carbamoyl, alkylsulfonyl, arylsulfonyl, sulfonamido and sulfamoyl groups wherein the substituents typically contain 1 to 42 carbon atoms. Such substituents can also be further substituted.

The materials for use in the invention can be used in any of the ways and in any of the combinations known in the art. Typically, the materials are incorporated in a silver halide emulsion and the emulsion coated as a layer on a support to form part of a photographic element. Alternatively, unless provided otherwise, they can be incorporated at a location adjacent to the silver halide emulsion layer where, during development, they will be in reactive association with development products such as oxidised colour developing agent. Thus, as used herein, the term "associated" signifies that the compound is in the silver halide emulsion layer or in an adjacent location where, during processing, it is capable of reacting with silver halide development products.

The photographic elements can be single colour elements or multicolour elements. Multicolour elements contain image dye-forming units sensitive to each of the three primary regions of the spectrum. Each unit can comprise a single emulsion layer or multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer.

- 17 -

A typical multicolour photographic element comprises a support bearing a cyan dye image-forming unit comprised of at least one red-sensitive silver halide emulsion layer having associated therewith at least one cyan dye-forming coupler, a magenta dye image-forming unit comprising at least one green-sensitive silver halide emulsion layer having associated therewith at least one magenta dye-forming coupler, and a yellow dye image-forming unit comprising at least one blue-sensitive silver halide emulsion layer having associated therewith at least one yellow dye-forming coupler. The element can contain additional layers, such as filter layers, interlayers, overcoat layers and subbing layers.

10 In the following discussion of suitable materials for use in the emulsions and elements that can be used in conjunction with this photographic element, reference will be made to Research Disclosure, September 1996, Item 38957, published by Kenneth Mason Publications, Ltd., Dudley House, 12 North Street, Emsworth, Hampshire PO10 7DQ, England, which will be identified hereafter by the term "Research Disclosure" and the Sections hereafter referred to are Sections of this Research Disclosure.

The emulsions can be surface-sensitive emulsions, i.e. emulsions that form latent images primarily on the surfaces of the silver halide grains, or the emulsions can form internal latent images predominantly in the interior of the silver halide grains. The emulsions can be negative-working emulsions, such as surface-sensitive emulsions or unfogged internal latent image-forming emulsions, or direct-positive emulsions of the unfogged, internal latent image-forming type, which are positive-working when development is conducted with uniform light exposure or in the presence of a nucleating agent.

25 Suitable emulsions and their preparation as well as methods of chemical and spectral sensitisation are described in Sections I and III-IV. Vehicles and vehicle related addenda are described in Section II. Dye image formers and modifiers are described in Section X. Various additives such as UV dyes, brighteners, luminescent dyes, antifoggants, stabilizers, light absorbing and scattering materials, coating aids, plasticizers, lubricants, antistats and matting

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- 20 -

The invention may be practised with any permanent high-boiling solvent known to be useful in the art, such as an aryl ester, such as dibutyl phthalate, diundecyl phthalate; phenols, such as p-dodecyl phenol, 2,4-di-isoamyl phenol: phosphates, such as trihexyl phosphate and tricresyl phosphate; alcohols, such as oleyl alcohol
5 and hexadecanol and amides such as diethyldodecanamide and dibutylacetanilide.

The resulting organic solution may then be mixed with an aqueous gelatin solution and the mixture passed through a mechanical mixing device suitable for high-shear or turbulent mixing generally suitable for preparing photographic emulsified dispersions, such as a colloid mill, homogenizer, microfluidizer, high-
10 speed mixer, ultrasonic dispersing apparatus, blade mixer, device in which a liquid stream is pumped at high pressure through an orifice or interaction chamber, Gaulin mill or blender to form small particles of the organic phase suspended in the aqueous phase. More than one type of device may be used to prepare the dispersions. The auxiliary organic solvent may then removed by evaporation,
15 noodle washing, or membrane dialysis. The dispersion particles preferably have an average particle size of less than $2\mu\text{m}$, generally from about 0.02 to $2\mu\text{m}$, more preferably from about 0.02 to $0.5\mu\text{m}$, especially from about 0.02 to $0.3\mu\text{m}$. These methods are described in detail in U.S. Patent Nos. 2,322,027, 2,787,544, 2,801,170, 2,801,171, 2,949,360 and 3,396,027.

20 Examples of suitable auxiliary solvents which can be used in the present invention include: ethyl acetate, isopropyl acetate, butyl acetate, ethyl propionate, 2-ethoxyethylacetate, 2-(2-butoxyethoxy) ethyl acetate, dimethylformamide, 2-methyl tetrahydrofuran, triethyl-phosphate, cyclohexanone, butoxyethyl acetate, methyl isobutyl ketone, methyl acetate, 4-methyl-2-pentanol, diethyl carbitol,
25 1,1,2-trichloroethane and 1,2-di-chloropropane.

The aqueous phase of the coupler dispersions for use in the invention preferably comprises gelatin as a hydrophilic colloid. This may be gelatin or a modified gelatin such as acetylated gelatin, phthalated gelatin or oxidized gelatin. Gelatin may be base-processed, such as lime-processed gelatin, or may be acid-
30 processed, such as acid-processed ossein gelatin. Other hydrophilic colloids may also

- 22 -

The materials for use in the invention may also be used in combination with filter dye layers comprising colloidal silver sol or yellow, cyan and/or magenta filter dyes, either as oil-in-water dispersions, latex dispersions or as solid particle dispersions. Additionally, they may be used with "smearing" couplers (e.g. as described in U.S. Patent Nos. 4,366,237, 4,420,556, 4,543,323 and in EP 96,570) Also, the compositions may be blocked or coated in protected form as described, for example, in Japanese Application 61/258,249 or U.S. Patent No. 5,019,492.

The materials for use in the invention may further be used in combination with image-modifying compounds such as "Developer Inhibitor-Releasing" compounds (DIRs). DIRs useful in conjunction with the compositions of the invention are known in the art and examples are described in U.S. Patent Nos. 3,137,578; 3,148,022; 3,148,062; 3,227,554; 3,384,657; 3,379,529; 3,615,506; 3,617,291; 3,620,746; 3,701,783; 3,733,201; 4,049,455; 4,095,984; 4,126,459; 4,149,886; 4,150,228; 4,211,562; 4,248,962; 4,259,437; 4,362,878; 4,409,323; 4,477,563; 4,782,012; 4,962,018; 4,500,634; 4,579,816; 4,607,004; 4,618,571; 4,678,739; 4,746,600; 4,746,601; 4,791,049; 4,857,447; 4,865,959; 4,880,342; 4,886,736; 4,937,179; 4,946,767; 4,948,716; 4,952,485; 4,956,269; 4,959,299; 4,966,835; 4,985,336 as well as in patent publications GB 1,560,240; GB 2,007,662; GB 2,032,914; GB 2,099,167; DE 2,842,063; DE 2,937,127; DE 3,636,824; DE 3,644,416 as well as the following European Patent Publications: 272,573; 335,319; 336,411; 346, 899; 362, 870; 365,252; 365,346; 373,382; 376,212; 377,463; 378,236; 384,670; 396,486; 401,612; 401,613.

Such compounds are also disclosed in "Developer-Inhibitor-Releasing (DIR) Couplers for Color Photography," C.R. Barr, J.R. Thirtle and P.W. Vittum in Photographic Science and Engineering, Vol.13, p.174 (1969). Generally, the developer inhibitor-releasing (DIR) couplers include a coupler moiety and an inhibitor coupling-off moiety (IN). The inhibitor-releasing couplers may be of the time-delayed type (DIAR couplers) which also include a timing moiety or chemical switch which produces a delayed release of inhibitor. Examples of typical inhibitor moieties are: oxazoles, thiazoles, diazoles, triazoles, oxadiazoles, thiadiazoles, oxathiazoles, thiatriazoles,

- 25 -

production of carbon dioxide, formaldehyde or other low molecular weight by-products. The groups are exemplified in EP 464,612, EP 523,451, U.S. 4,146,396, Japanese Kokai 60-249148 and 60-249149.

It is also contemplated that the concepts of the present invention may be employed to obtain reflection colour prints as described in Research Disclosure, November 1979, Item 18716, available from Kenneth Mason Publications, Ltd, Dudley Annex, 12a North Street, Emsworth, Hampshire P0101 7DQ, England. Materials of the invention may be coated on pH adjusted support as described in U.S. Patent No. 4,917,994; on a support with reduced oxygen permeability (EP 553,339); with epoxy solvents (EP 64,961); with nickel complex stabilisers (U.S. Patent Nos. 4,346,165, 4,540,653 and 4,906,559 for example); with ballasted chelating agents such as those in U.S. Patent No. 4,994,359 to reduce sensitivity to polyvalent cations such as calcium and with stain reducing compounds such as described in U.S. Patent No. 5,068,171. Other compounds useful in combination with the invention are disclosed in Japanese Published Applications described in Derwent Abstracts having accession numbers as follows: 90-072,629, 90-072,630; 90-072,631; 90-072,632; 90-072,633; 90-072,634; 90-077,822; 90-078,229; 90-078,230; 90-079,336; 90-079,337; 90-079,338; 90-079,690; 90-079,691; 90-080,487; 90-080,488; 90-080,489; 90-080,490; 90-080,491; 90-080,492; 90-080,494; 90-085,928; 90-086,669; 90-086,670; 90-087,360; 90-087,361; 90-087,362; 90-087,363; 90-087,364; 90-088,097; 90-093,662; 90-093,663; 90-093,664; 90-093,665; 90-093,666; 90-093,668; 90-094,055; 90-094,056; 90-103,409; 83-62,586 and 83-09,959.

Any silver halide combination can be used for the photographic element, such as silver chloride, silver chlorobromide, silver chlorobromiodide, silver bromide, silver bromiodide, or silver chloriodide. In cases where the emulsion composition is a mixed halide, the minor component may be added in the crystal formation or after formation as part of the sensitisation or melting. The shape of the silver halide emulsion grain can be cubic, pseudo-cubic, octahedral, tetradecahedral or tabular. The emulsions may be precipitated in any suitable

- 34 -

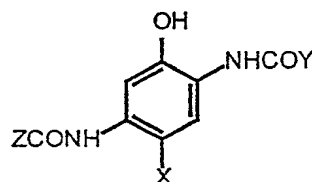
The results show that the couplers I-1 and I-2 of this invention are comparable in activity to the comparison couplers CC1 and CC2, and give dyes with adequately deep hue. The thermal dark stability of the image dye from the comparison coupler CC1 is good, and superior to that of the comparison coupler
5 CC2, but its light stability is poor. The dyes from the inventive couplers I-1 and I-2 retain the excellent dark stability displayed by the analogous dyes from CC1, and also demonstrate good light stability, superior to that of the image dye from CC2.

Comparison coupler CC2 is already well known as a commercially
10 important component of photographic colour paper products and the image dyes from the inventive couplers are superior to those of CC2 in terms of resistance to decomposition by both light and heat.

The invention has been described in detail with particular reference to certain preferred embodiments thereof, but it will be understood that variations
15 and modifications can be effected within the claims of the invention.

Claims:

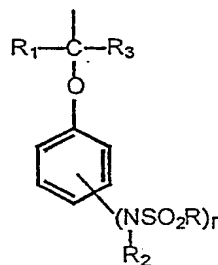
1. A photographic element comprising at least one silver halide emulsion layer having associated therewith a phenolic cyan dye-forming coupler of formula (I)



(I)

wherein

X is hydrogen or a group that can be split off by the reaction of the coupler with an oxidised colour developing agent, and
one of Y and Z is the group



wherein

each R is independently an unsubstituted or substituted alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted;

R₁ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

R₂ is an unsubstituted or substituted alkyl or aryl group or a 5-10 membered heterocyclic ring which contains one or more heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted;

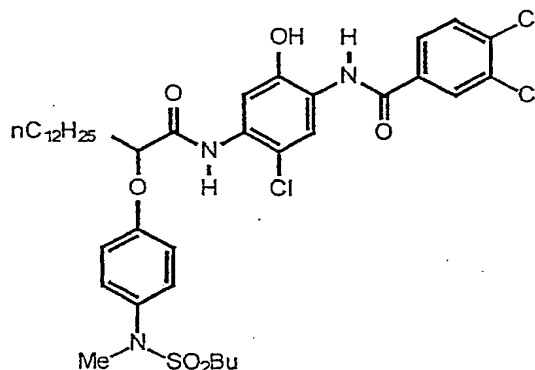
R₃ is hydrogen or an unsubstituted or substituted alkyl or aryl group,

n is 1 or 2, and each group -N(R₂)SO₂R is in the ortho or para position,

the other of Y and Z is a fluoro-substituted alkyl group or an unsubstituted or substituted aryl group or a 5-10 membered heterocyclic ring which contains one or more

heteroatoms selected from nitrogen, oxygen and sulfur, which ring is unsubstituted or substituted, provided that (a) when R_2 is an unsubstituted benzyl group, n is 1 and $-N(R_2)SO_2R$ is in the ortho position, R may not be a pyridyl group, and (b) at least one of R , R_1 , R_2 , X and Y or Z is or includes a ballast group.

- 5 2. An element according to claim 1 wherein R , R_1 and R_2 are independently an unsubstituted or substituted alkyl group.
3. An element according to either of the preceding claims wherein each of R and R_2 is a lower alkyl group.
4. An element according to any one of the preceding claims wherein R_1 is an alkyl
- 10 group having at least 8 carbon atoms.
5. An element according to any one of the preceding claims wherein R_3 is hydrogen.
6. An element according to any one of the preceding claims wherein n is 1 and the group $-N(R_2)SO_2R$ is in the para position.
7. An element according to any one of the preceding claims wherein the group Z
- 15 contains the $-N(R_2)SO_2R$ substituent and the group Y is an unsubstituted or substituted aryl group.
8. An element according to any one of the preceding claims wherein the cyan dye-forming coupler has the structure



PATENT COOPERATION TREATY

EASTMAN KODAK CO.
AUG 21 2000
PATENT LEGAL STAFF

From the:
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

**ENTERED IN
PCMASTER**

PCT

To:

HAILE, Helen C. et al
KODAK LIMITED
Patent Department
Headstone Drive
HARROW, MIDDLESEX HA1 1PY
GRANDE BRETAGNE

COPY SENT

DATE 11/08/2000

ROC ☒ KAG ☐

KP ☐

COVER 11527

TA 09

DOCKET #

79888/11527

FIG. 6

19828147-6

WRITTEN OPINION

(PCT Rule 66)

Date of mailing
(day/month/year) 11.08.2000

Applicant's or agent's file reference
79888/11527

REPLY DUE within 3 month(s)
from the above date of mailing

International application No.
PCT/GB99/04360

International filing date (day/month/year)
22/12/1999

Priority date (day/month/year)
22/12/1998

International Patent Classification (IPC) or both national classification and IPC
G03C7/34

Applicant
EASTMAN KODAK et al.

1. This written opinion is the **first** drawn up by this International Preliminary Examining Authority.
2. This opinion contains indications relating to the following items:
 - I ☒ Basis of the opinion
 - II ☐ Priority
 - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
 - IV ☐ Lack of unity of invention
 - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability: citations and explanations supporting such statement
 - VI ☐ Certain document cited
 - VII ☒ Certain defects in the international application
 - VIII ☒ Certain observations on the international application
3. The applicant is hereby **invited to reply** to this opinion.

When? See the time limit indicated above. The applicant may, before the expiration of that time limit, request this Authority to grant an extension, see Rule 66.2(d).

How? By submitting a written reply, accompanied, where appropriate, by amendments, according to Rule 66.3. For the form and the language of the amendments, see Rules 66.8 and 66.9.

Also: For an additional opportunity to submit amendments, see Rule 66.4.
For the examiner's obligation to consider amendments and/or arguments, see Rule 66.4 bis.
For an informal communication with the examiner, see Rule 66.6.

If no reply is filed, the international preliminary examination report will be established on the basis of this opinion.
4. The final date by which the international preliminary examination report must be established according to Rule 69.2 is: 22/04/2001.

Name and mailing address of the international preliminary examining authority:



European Patent Office
D-80298 Munich
Tel. +49 89 2399 - 0 Tx: 523656 epmu d
Fax: +49 89 2399 - 4465

Authorized officer / Examiner

Binder, R

Formalities officer (incl. extension of time limits)
Kammerer, R
Telephone No. +49 89 2399 8084



I. Basis of the opinion

1. This opinion has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this opinion as "originally filed"*):

Description, pages:

1-34 as originally filed

Claims, No.:

1-12 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

3. This opinion has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:

V. Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims 1-7,10-12 NO
Inventive step (IS)	Claims
Industrial applicability (IA)	Claims

2. Citations and explanations

see separate sheet

VII. Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

see separate sheet

Reference is made to the following documents:

D1: US-A-4362810
D2: GB-A-2070000
D3: US-A-4299914
D4: Database WPI, Week 198422, AN 1984-136665 & JP-A-59069755
D5: US-A-4214396

CONCERNING SECTION V (CITATIONS AND EXPLANATIONS SUPPORTING THE STATEMENT WITH REGARD TO NOVELTY, INVENTIVE STEP OR INDUSTRIAL APPLICABILITY):

The subject-matter of Claims 1 to 7 and 10 to 12 lacks novelty.

Document 1 describes a method for forming a cyan image by developing an imagewise exposed silver halide emulsion layer with an aromatic primary amine colour developing agent in the presence of a 2,5-diacylaminophenol cyan coupler containing a substituted alkylsulfonylamino terminal moiety in the 2- or 5- position of the molecule (see Claim 1). The coupler is preferably represented by a formula (see Claims 2 and 4) which overlaps with formula (I) of Claim 1 of the present application. Coupler 25 of Document 1 (see table II on columns 7 and 8) satisfies this formula.

Document 2 describes a cyan coupler of a formula which overlaps with formula (I) of Claim 1 of the present application (see Claim 9 of Document 1), a method of forming a cyan dye image (see Claim 1) which comprises developing an imagewise exposed silver halide emulsion layer with an aromatic primary amine colour developing agent in the presence of said coupler and a colour photographic material (see Claim 10) having a silver halide emulsion layer containing such a cyan coupler. Coupler 3 of Document 2 (see table I on page 3) satisfies this formula.

Document 3 describes a silver halide photographic material (see Claim 14) having a silver halide emulsion layer coated on a support which layer contains a cyan coupler of a formula which overlaps with formula (I) of Claim 1 of the present application and a method (see Claim 1 of Document 3) for forming a cyan dye image by developing an imagewise exposed silver halide photographic material with an aromatic primary amine colour developing agent in the presence of said coupler. Coupler 18 of Document 3 (see the table on columns 5 and 6) satisfies this formula.

Document 4 describes a photographic cyan phenolic coupler having a benzamide group at the 2-position of the phenolic nucleus and an acylamino group at the 5-position of the phenolic nucleus (see the English abstract). Coupler 19 of Document 3 (see page 4) satisfies formula (I) of Claim 1 of the present application.

Documents 1 to 4 as a whole thus describe couplers, photographic elements and processes comprising all features of independent Claims 1, 11 and 12 of the present application. It is not explicitly mentioned in those documents that the cyan couplers should be incorporated in elements as described in Claim 10 of the present application. However, an application in colour photographic materials is suggested and a person skilled in the art would seriously contemplate to use the above-mentioned cyan couplers of Documents 1 to 4 in multicolour photographic elements such as those described in Claim 10 of the present application (cf also lines 5 to 51 of Document 5).

The above-mentioned couplers of Documents 1 to 4 satisfy one or more of dependent Claims 2 to 7 of the present application

Hence Claims 1 to 7 and 10 to 12 do not meet the requirements of Articles 33 (2) PCT.

CONCERNING SECTION VII (CERTAIN DEFECTS IN THE INTERNATIONAL APPLICATION):

The following defects in the form or contents of the international application have been noted:

1. Contrary to the requirements of Rule 5.1(a)(ii) PCT, the relevant background art disclosed in Documents 1 and 3 to 5 is not mentioned in the description, nor are these documents identified therein.
2. In some countries or regions, such as in Europe, the expression "the disclosure of which is incorporated by reference" and a reference to the "spirit of the invention" are regarded as introducing ambiguity.
3. In lines 15 and 16 of page 16 the terms "material of the invention" and "inventive materials" should preferably be replaced by, e.g., "couplers of formula (I)".

CONCERNING SECTION VIII (CERTAIN OBSERVATIONS ON THE INTERNATIONAL APPLICATION):

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

1. Claim 4 has no clear support in the description since in the description (see, e.g., lines 14 to 16 of page 5) it is not mentioned that it is R_1 that should be an alkyl group having at least 8 carbon atoms.
2. Claim 10 comprises all the features of Claim 1 but is not appropriately formulated as a claim dependent on the latter (Rule 6.4 PCT).
3. According to lines 4 to 6 of page 7 it is important that groups R , R_1 , R_2 , X and Y or Z are selected so as to adequately ballast the coupler and the resulting dye in the organic solvent in which the coupler is dispersed. This is not reflected in the independent claims.

**WRITTEN OPINION
SEPARATE SHEET**

International application No. PCT/GB99/04360

4. Coupler 1-10 (see page 11) presented as an example illustrating the invention (see line 1 of page 8) does not satisfy formula (I) of Claim 1.

PCT

REC'D 27 MAR 2001

WIPO PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

3

Applicant's or agent's file reference 79888/11527	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/GB99/04360	International filing date (day/month/year) 22/12/1999	Priority date (day/month/year) 22/12/1998
International Patent Classification (IPC) or national classification and IPC G03C7/34		
Applicant EASTMAN KODAK et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.


2. This REPORT consists of a total of 4 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 13 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 30/06/2000	Date of completion of this report 23.03.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Binder, R Telephone No. +49 89 2399 8951



INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/04360

I. Basis of the report

1. This report has been drawn on the basis of *(substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments (Rules 70.16 and 70.17).)*:

Description, pages:

1,3,6-10,13-15,18, as originally filed
19,21,23,24,
26-33

2,4,5,11,12,16,17, as received on 03/11/2000 with letter of 02/11/2000
20,22,25,34

Claims, No.:

9-12 as originally filed

1-8 as received on 03/11/2000 with letter of 02/11/2000

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/GB99/04360

- ☐ the description, pages:
☐ the claims, Nos.:
☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-12
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-12
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-12
	No:	Claims	

2. Citations and explanations
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

CONCERNING SECTION V (CITATIONS AND EXPLANATIONS SUPPORTING THE STATEMENT WITH REGARD TO NOVELTY, INVENTIVE STEP OR INDUSTRIAL APPLICABILITY):

1. None of the available documents describes an element comprising all features of Claims 1 or 10, a process of forming an image comprising all features of Claim 11 or a coupler comprising all features of Claim 12 of the present application or provides a general disclosure that would inevitably lead to such an element, process or coupler. The subject-matter of independent Claims 1 and 10 thus meets the requirements of Article 33 (2) PCT.
2. The closest state of the art is Document 1 (US-A-4362810). With the exception of compound 25, which no longer satisfies formula (I) of Claim 1 of the present application, there is no hint that sulfonamides having an alkyl, aryl or heterocyclic ring attached to the nitrogen may provide advantageous effects. Document 1 rather suggests the use of sulfonamides lacking a substituent on the nitrogen. The subject-matter of independent Claims 1, 10, 11 and 12 thus also meets the requirements of Article 33 (3) PCT.
3. The dependent Claims 2 to 9 describe advantageous embodiments of the elements of Claim 1 and thus likewise meet the requirements of Articles 33 (2) and (3) PCT.

CONCERNING SECTION VIII (CERTAIN OBSERVATIONS ON THE INTERNATIONAL APPLICATION):

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

Claim 10 comprises all the features of Claim 1 but is not appropriately formulated as a claim dependent on the latter (Rule 6.4 PCT). The applicant has indicated that he wishes to retain this claim in its present format.

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C. 20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 07 August 2000 (07.08.00)	Applicant's or agent's file reference 79888/11527
International application No. PCT/GB99/04360	Priority date (day/month/year) 22 December 1998 (22.12.98)
International filing date (day/month/year) 22 December 1999 (22.12.99)	Applicant CLARKE, David et al

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
30 June 2000 (30.06.00)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was
☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<p style="text-align: center;">The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No.: (41-22) 740.14.35</p>	<p>Authorized officer Zakaria EL KHODARY</p> <p>Telephone No.: (41-22) 338.83.38</p>
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